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CCCLXIV.—*Examination of the Volatile Oils from* Xanthorrhœa arborea, X. hastilis, *and* X. reflexa.

By Hedley Herbert Finlayson.

Rennie, Cooke, and Finlayson (J., 1920, **117**, 338) have described the examination of two species of *Xanthorrhœa* resin from Kangaroo Island, and of the resin of *X. Preissii* from West Australia. The present paper is an account of the examination of the resins of two other species from New South Wales, *viz.*, *X. arborea* and *X. hastilis*, and of *X. reflexa* (a species closely resembling *X. Preissii*) from West Australia.

In each case the volatile oil was obtained, in the way previously described, by the distillation of an alkaline solution of the resin with steam and was separated into phenolic and non-phenolic portions by shaking it with a solution of sodium hydroxide.

Examination of X. arborea.—*Volatile oil.* The specimen of resin used was fairly clean and comparatively free from husks and gravel —the individual flakes of resin were dark brownish-red and nearly opaque.

The oil, the yield of which amounted to about 1%, was dark brown and of agreeable spicy odour recalling that of the oil from *X. Tateana*.

The non-phenolic portion from 15 g. of oil amounted to 4·5 g., was very viscous and dark brown, and appeared to contain all the sweet-smelling constituents of the original oil. When an attempt was made to distil it at 18 mm. the liquid frothed excessively owing to the presence of sticky, resinous, scarcely volatile substances, and these were therefore removed by steam distillation. The light yellow rectified oil recovered from this distillate (now reduced to 2·5 g.) distilled at 115—190°/18 mm. and appeared to contain a number of substances about which very little could be learned owing to the small quantity of material available; the odour, however, was indistinguishable from that of the corresponding fractions of the oils from *X. Tateana* and the yellow resin from Kangaroo Island (*loc. cit.*).

The 10·5 g. of phenols, also dark brown, when fractionated at 18 mm., gave 7·5 g. from 155—165° and about 1 g. from 165—190°, leaving 1·5 g. of a dark brown resinous residue.

The first two fractions slowly solidified almost completely, and from them, by recrystallisation from dilute alcohol, large proportions of pure pæonol and hydroxypæonol of m. p. 49° and 80°, respectively, were obtained.

The approximate composition of the oil from this species is

therefore: Pæonol 50%, hydroxypæonol 6·5%, non-phenolic substances of b. p. 115—190°/18 mm., including the fragrant principle of the resin, 17%, and dark-coloured resinous substances, partly soluble and partly insoluble in alkali, and presumably formed by oxidation and polymerisation of other constituents, subsequent to the first distillation, 26·5% (diff.).

Acids. The acids, which in the species previously examined appeared to be loosely attached to the complex resin molecule and were easily split off by a short digestion with dilute alkali, were again tested for in the present instance, but without success.

The method used was identical with that previously described (*loc. cit.*), but on evaporation of the ethereal extract only a very small quantity of a dark oily substance was obtained from which neither *p*-hydroxybenzaldehyde, *p*-coumaric acid, nor any other crystalline acid could be separated.

Examination of X. hastilis.—The specimen of the resin of this species was much less homogeneous than that of *X. arborea*, and the material insoluble in alcohol—husks, sand, etc.—amounted to 25% of the whole. The individual flakes of resin varied in colour from a dull mustard to a brownish-yellow.

Volatile oil. The yield of oil calculated on the pure resin taken was 1·56%. It was a pale yellow liquid of pleasant odour differing entirely from that of *X. arborea*.

Phenols. 23·5 G. of oil, on treatment with alkali, yielded 1·16 g. of brown liquid phenols which, even when cooled strongly and seeded with pæonol and hydroxypæonol, showed no signs of crystallisation.

The alcoholic solution gave with ferric chloride a reddish-brown coloration, and with cold nitric acid a dull green coloration developed which changed rapidly to yellow on warming. Pæonol and hydroxypæonol appeared to be entirely absent, and in this respect the resin differs from all others previously examined.

Non-phenols. After thorough drying over anhydrous potassium carbonate the non-phenols were carefully fractionated under 18 mm. After three series the following fractions were obtained: (I) up to 130°, 3·0 g.; (II) 130—140°, 1·5 g.; (III) 140—150°, 10·0 g. The dark sticky residue weighed 6—7 g.

Fraction I had a very pleasant rose-like smell, changing on shaking with dilute chromic acid to the penetrating smell of citronellal, and on acetylation acetates were formed closely resembling citronellyl acetate in odour—so that the presence of citronellol seemed fairly certain.

In an attempt to prove the presence of this alcohol, the acid phthalic esters were prepared and converted into the corresponding

silver salts; from these, by repeated crystallisation from boiling methyl alcohol, a fraction was obtained of m. p. 123—125° which contained 27·55% Ag as against 26·23% required for the citronellyl compound, 26·4% for the geranyl, and 27·76% for the cinnamyl phthalate.

Fraction III, after several redistillations under low pressure, and after long standing, solidified almost completely, and when freed from oily impurities by long and heavy pressure between blotting paper, the solid had m. p. 32—33° and b. p. 142—144°/18 mm. and 126—128°/5—7 mm. It was proved to be cinnamyl alcohol by its behaviour on oxidation, by the preparation of the dibromide of m. p. 72—73°, and by comparison with an authentic sample.

Fraction II also consisted largely of cinnamyl alcohol contaminated with small quantities of the lower-boiling, fragrant alcohols.

The oil from this species therefore approximately consists of fragrant, low-boiling alcohols 8% (probably largely citronellol), cinnamyl alcohol 53%, phenols 5%, and resinification products.

The resin was examined for acids in the same way as in previous cases, but oily, indefinite substances only were obtained, and these in small quantity.

Examination of X. reflexa.—*Volatile oil.* The specimen of resin examined was a very homogeneous one, picked out from 20 lb. of the rough material and consisting of large tears free from husk and woody matter. It differed from the resin of *X. Preissii*, with which it is botanically closely associated, in its much darker colour, which, however, is less noticeable in powdered specimens.

The yield of oil was 6·86%. It was dark brown and of pleasant smell. 68·59 G. of it were treated with alkali and separated into a phenolic and a non-phenolic portion.

Phenolic portion. The portion (48 g.) soluble in alkali was systematically fractionated at a pressure of 18 mm., with the following results: (1) up to 150°, 2·0 g.; (2) 150—160°, 41·0 g.; (3) 160—175°, 1·75 g.; (4) 175—185°, 1·25 g. On standing, fractions 1 and 3 solidified partly, 2 and 4 completely.

Fraction 1, on prolonged pressure between blotting-paper, gave 1 g. of crystalline pæonol. The oily portion recovered from the paper by extraction with ether, and still containing a small quantity of pæonol, was a phenol of lower boiling point with a creosote-like smell. Its colour reaction with ferric chloride was identical with that of pæonol and it yielded a benzoate readily, which, however, refused to crystallise. The quantity was insufficient for further examination.

Fraction 2, on recrystallisation from alcohol, yielded almost its own weight of pure pæonol, m. p. 49°.

Fraction 4 similarly yielded hydroxypæonol, and the intermediate fraction consisted of a mixture of the two compounds, pæonol predominating.

Non-phenolic portion. After removal of the solvent from the benzene washings from the treatment of the original oil with alkali, 19 g. of dark brown, aromatic-smelling, non-phenols were obtained which on fractionation at 18 mm. gave the following results: (1) up to 100°, 2·25 g.; (2) 100—200°, 2·20 g.; (3) 200—210°, 11·75 g. The residue weighed 1·5 g.

Fraction 1 consisted essentially of benzaldehyde, which was identified by oxidation to benzoic acid on exposure to air and by preparation of the phenylhydrazone of m. p. 155°. The smell was modified somewhat by the presence of a small quantity of the ketone mentioned below.

Fraction 2 consisted of a pale yellow, highly refractive liquid of powerful aromatic smell recalling strongly that of some acacia blossoms. Small quantities of benzaldehyde and of the high-boiling compound of fraction (3) were present, but the chief constituent appeared to be a saturated aromatic ketone, yielding a pale yellow phenylhydrazone of m. p. 114° and a liquid oxime. On oxidation by prolonged boiling with 5% chromic acid mixture, a greasy neutral product was formed, together with a small yield of a mixture of crystalline acids, a partial separation of which was effected by steam distillation. From the non-volatile portion, by repeated crystallisation from dilute alcohol, long, pale yellow needles of m. p. 180·5° (corr.) were obtained, which, when heated with soda–lime, developed an unmistakable smell of anisole—a mixture of equal parts of this acid and of a specimen of anisic acid melted at 183°. The acid volatile with steam was not homogeneous and was obtained in very small quantity only: it melted indefinitely at 140—145° and gave a yellow insoluble ferric salt. The quantity of the ketone available was insufficient for further work.

Fraction 3 solidified completely on standing and after recrystallisation from alcohol gave 10 g. of white, crystalline material, m. p. 68—69°, $[\alpha]_D^{13^\circ} + 55{\cdot}57^\circ$ (in 10% benzene solution). The substance was identical with that previously isolated from the corresponding fraction of *X. Preissii*.

The approximate composition of the volatile oil from *X. reflexa* is therefore pæonol, 62·8%; hydroxypæonol, 2·9%; phenols of lower boiling point than the above, 1·5%; benzaldehyde, 3·2%; an aromatic ketone containing one *p*-methoxyphenyl group, 3%;

the compound of m. p. 68—69° previously isolated from *X. Preissii*, 17·5%; resinous residues, loss, and undetermined, 9·1%.

The compound of m. p. 68—69°, to which the formula $C_{13}H_{12}O_2$ was provisionally ascribed, has now been found to possess optical activity, a fact which was previously overlooked. Although many analyses have been made, the figures obtained are not decisive; they appear, however, in the main to indicate the formula $C_{14}H_{14}O_2$ rather than $C_{13}H_{12}O_2$. The substance is extremely stable and so far no derivatives have been prepared which throw any light on its relationships. Experiments are being undertaken to accumulate a larger quantity than has yet been available with a view to further examination.

The products from *X. Preissii* and *X. reflexa*, which are botanically closely allied, are very similar chemically and differ from those of any other species in containing the unidentified substance above referred to.

In conclusion I desire to thank Professor E. H. Rennie, who has maintained a most helpful interest in this work, and also Mr. F. K. Carter, B.Sc., and Mr. J. G. Wood, B.Sc., who gave valuable assistance.

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[*Received, May 11th*, 1926.]

CCCLXV.—*Olefinic Terpene Ketones from the Volatile Oil of Flowering* Tagetes glandulifera. *Part II.*

By THOMAS GILBERT HENRY JONES.

THE structures assigned by Jones and Smith to $\gamma\eta$-dimethyl-Δ^{α}-octen-ε-one and tagetone, the two olefinic terpene ketones isolated from the volatile oil of *Tagetes glandulifera* (J., 1925, **127**, 2530), depended primarily on the identity of the saturated ketone—the common product of their reduction—and of the ketonic acid resulting from oxidation of the former with $\gamma\eta$-dimethyloctan-ε-one and β-*iso*valeryl-α-methylpropionic acid, respectively.

The saturated ketone and the ketonic acid have now been synthesised by the ketonic hydrolysis of the products of interaction of ethyl sodio*iso*valerylacetate with (*a*) *sec.*-butyl iodide, and (*b*) ethyl α-iodopropionate.

The properties of $\gamma\eta$-dimethyl-Δ^{α}-octen-ε-one and tagetone have been further examined. Agitated for 2 hours with 70% sulphuric acid at about 100°, $\gamma\eta$-dimethyl-Δ^{α}-octen-ε-one undergoes profound

decomposition with production of methyl ethyl ketone, methyl *iso*butyl ketone, and *iso*valeric acid. The reaction, no doubt, involves hydrolysis of $\gamma\eta$-dimethyl-Δ^{β}-octen-ε-one, formed by the shifting of the double bond of the original ketone to the β-position. The isomeric ketone could not, however, be isolated during the course of the reaction. Although tagetone is almost entirely resinified by heating with alcoholic potash, methyl *iso*butyl ketone, presumably a product of its hydrolysis, is formed in small quantity. No evidence of ring condensation in the ketones was obtained.

The tendency of tagetone to pinacol formation is marked. The pinacol and the substance $C_{10}H_{18}O$ previously obtained by the action of sodium in moist ether (*loc. cit.*) are also produced with zinc and acetic acid as reducing agent; zinc dust and alcoholic potash gave rise only to the pinacol, which is the sole product also of electrolytic reduction (*loc. cit.*).

The substance $C_{10}H_{18}O$ has now been proved to be an alcohol, which it is proposed to designate tagetol. Its density (0·8524) is somewhat low in comparison with that of tagetone (0·8803), a fact probably to be accounted for by partial polymerisation of the latter during distillation. Compared with tagetone, both tagetol and the pinacol are stable substances, distilling under reduced pressure with but little resinification. Tagetol reacts readily with acetic and phthalic anhydrides, but on regeneration from the liquid acid phthalate suffers considerable loss by resinification. Attempts to dehydrate tagetol with a view to the production of an olefinic terpene were but partly successful; heated at 180° with potassium hydrogen sulphate, the alcohol was mostly recovered unchanged, whilst the quantity of hydrocarbon produced by warming with phosphoric oxide was too small to permit of its characterisation.

The preservation of the two ethylenic linkings of tagetone during reduction, as shown by the analysis and the iodine value (336, equivalent to four atoms of iodine) of tagetol, indicates that the former does not function as an αβ-ketone, and lends support to the view (*loc. cit.*) that tagetone is to be regarded as comprising, in its main reactions, the group $\cdot CO\cdot CH_2\cdot C(:CH_2)\cdot CH:CH_2$ in preference to the alternative $\cdot CO\cdot CH:CMe\cdot CH:CH_2$. As, however, the latter group provides equally well for the fundamental property of capacity for enolisation, it is possible that the structure of the ketone is fully and more correctly represented by the tautomeric systems $\cdot CO\cdot CH_2\cdot C(:CH_2)\cdot CH:CH_2 \rightleftharpoons \cdot C(OH):CH\cdot C(:CH_2)\cdot CH:CH_2 \rightleftharpoons \cdot CO\cdot CH:CMe\cdot CH:CH_2$, whilst $\cdot CH(OH)\cdot CH_2\cdot C(:CH_2)\cdot CH:CH_2$ and $\cdot CH(OH)\cdot CH:CMe\cdot CH:CH_2$ represent derived isomeric tagetols.

The characteristics recently ascribed to the volatile oil of *T. minuta* (*Bull. Imp. Inst.*, 1924, **22**, 3, 279) in conjunction with the

observation already made (Part I, *loc. cit.*) in reference to the oil of *T. petula* would indicate that tagetone or allied ketones are common to or characteristic of the flower oils of the genus *Tagetes*.

It is proposed to continue, as opportunity offers, the examination of the reactions of tagetone and tagetol.

Experimental.

Synthesis of γη-Dimethyloctan-ε-one.—Ethyl *iso*valerylacetate (25 g.) was heated under reflux on the water-bath with a solution of 3·4 g. of sodium in 150 c.c. of absolute alcohol and 27 g. of *sec.*-butyl iodide for 8 hours; the alkaline reaction had then disappeared. The excess of alcohol was expelled, and *ethyl* sec.-*butyl*-iso*valerylacetate*, b. p. 133°/24 mm. (Found: C, 68·4; H, 10·3. $C_{13}H_{24}O_3$ requires C, 68·4; H, 10·5%), and the unchanged *iso*-valerylacetic ester were recovered by extraction with ether and separated by fractional distillation. The former (15 g.) was boiled for 15 hours with 300 c.c. of 10% alcoholic potash. (Hydrolysis by this reagent or by dilute sulphuric acid [1 : 3] appears to take place with difficulty.) *γη-Dimethyloctan-ε-one* was then isolated by steam distillation and, after fractional distillation, had b. p. 187°/760 mm., $d^{15·5°}$ 0·8190, $n_D^{20°}$ 1·4190—constants agreeing closely with those of the reduction product of the ketones of the flower oil, to which the constitution of γη-dimethyloctan-ε-one was assigned (*loc. cit.*) (Found: C, 76·6; H, 12·7. $C_{10}H_{20}O$ requires C, 76·9; H, 12·8%). The semicarbazones of the synthetic and the reduction product melted singly and in admixture at 91·5°.

Synthesis of β-iso*Valeryl-α-methylpropionic Acid.*—A solution of 3·4 g. of sodium in 150 c.c. of absolute alcohol was heated under reflux with 25 g. of ethyl *iso*valerylacetate and 33 g. of ethyl α-iodopropionate until neutral (8 hours). The product (22 g.), isolated by extraction with ether and distillation, had b. p. 167—169°/26 mm. (Found: C, 61·4; H, 8·6. $C_{14}H_{24}O_5$ requires C, 61·7; H, 8·8%). On being boiled for 48 hours with alcoholic potash, it gave β-*iso*valeryl-α-methylpropionic acid, b. p. 169—170°/24 mm. (Found: C, 62·4; H, 9·3%), the semicarbazone of which did not depress the m. p. (166°) of the semicarbazone of the ketonic acid obtained by the oxidation of γη-dimethyl-Δ^{α}-octen-ε-one. (The m. p. was recorded in Part I, *loc. cit.*, as 165°. The purest sample melts at 166°.)

Decomposition of γη-Dimethyl-Δ^{α}-octen-ε-one with 70% Sulphuric Acid.—A well-agitated mixture (20 g.) of γη-dimethyl-Δ^{α}-octen-ε-one and 100 c.c. of 70% sulphuric acid was heated under reflux on the water-bath for 2 hours, and the product steam-distilled. The distillate was extracted repeatedly with ether, and the extract shaken

with dilute alkali solution. The alkaline extract, on acidification and steam-distillation, gave a small quantity of *iso*valeric acid, which was identified by means of the silver salt and the anilide, m. p. 110—111°.

The residual ethereal extract, on distillation, gave two main fractions consisting essentially of methyl ethyl ketone (semicarbazone, m. p. 135°) and methyl *iso*butyl ketone (semicarbazone, m. p. 132°), respectively. A third small fraction (2 c.c.), collected at 180—190°/760 mm., was mainly composed, apparently, either of the original ketone or an isomeride, but the quantity available was too small for identification.

Owing to the small amount of $\gamma\eta$-dimethyl-Δ^{α}-octen-ε-one occurring in the essential oil, it was not possible to investigate this reaction further.

Decomposition of Tagetone by Alcoholic Potassium Hydroxide.—On steam distillation of the resinous mass resulting from treatment of 50 g. of tagetone under reflux with boiling alcoholic potash, a small amount (approx. 2 c.c.) of methyl *iso*butyl ketone was obtained. It was identified by means of its semicarbazone, m. p. 132°.

The author wishes to thank Mr. F. Berry Smith for assistance in several of the analyses recorded.

UNIVERSITY OF QUEENSLAND,
BRISBANE. [*Received, May 17th*, 1926.]

CCCLXVI.—*Melting-point Curves of Optical Isomerides in the Camphor Series.*

By JOHN D. M. ROSS and IAN C. SOMERVILLE.

THE problem as to the existence of racemic compounds, when two optical isomerides are mixed in equal quantities, was not placed on a satisfactory footing until Roozeboom (*Z. physikal. Chem.*, 1899, **28**, 494) studied the question from the point of view of the phase rule. He showed that there were three main types of curve to be expected: (1) the mixed-crystal curve, which would be a continuous curve joining the melting points of the two isomerides and in its simplest form would be a straight line; (2) a curve consisting of two parts giving a minimum of temperature at the point of intersection; and (3) a curve giving two minima (eutectic points) and a maximum point. Group 1 represents the pseudo-racemic mixed crystal, but does not preclude the existence of a racemic compound. Group 2 represents a simple mixture of *d*- and *l*-isomerides, the so-called *d*- and *l*-conglomerate. Group 3 represents the definite formation of a racemic compound.

Whilst the general shape of the melting-point curve of such

isomerides as have been studied has frequently been commented on, an exact mathematical analysis of the curves has not often been attempted. Kremann (*Monatsh.*, 1904, **25**, 1215) has shown how the degree of dissociation of the racemic compound may be calculated, and so a definite statement may be made as to the amount of racemic compound present in the liquid state. The calculations employed are not entirely free from objection, as is pointed out by Kremann himself, but they serve to give a very good indication of the correct result. The method has been applied by Findlay and Hickmans (J., 1907, **91**, 905) to the investigation of the melting-point curve of menthyl mandelate.

Washburn and Read (*Proc. Nat. Acad. Sci.*, 1915, **1**, 191) have suggested a formula which should yield the melting-point curve for so-called "ideal" solutions. As mixtures of optical isomerides fulfil the conditions of such "ideal" solutions more exactly than any other mixtures, it was suggested that the melting-point curves might be investigated from this point of view. A comparison of the results obtained by the Washburn and Read formula, by the van 't Hoff formula, and by the Raoult freezing-point law will be discussed in the course of this investigation. It should also be mentioned that van Laar (*Z. physikal. Chem.*, 1908, **63**, 216; 1908, **64**, 257; 1909, **66**, 197) has worked out a mathematical treatment of the possible curves in great detail, starting from the fundamental relationships given by the thermodynamic potential. From the evidence already accumulated, it seemed unlikely that a definite answer could be given to the question as to whether a racemic compound should exist in the liquid state apart from considerations of the molecular nature of the optical isomerides. If, for example, a molecule of *d*-isomeride shows a tendency to unite with another molecule of *d*-isomeride to give an associated molecule represented by 2*d*, then it might be expected that a molecule of *d*-isomeride would unite with one of *l*-isomeride to give a racemic compound analogous to the associated 2*d* molecule. If, on the other hand, the *d*-isomeride shows little tendency to associate with itself, then we might expect that the racemic compound, if formed, would be largely dissociated into its components. To test these conclusions, a number of related substances of various types in the camphor series were investigated, *viz.*:

d- and *l*-Borneol	Alcohol.
d- and *l*-Camphor	Ketone.
d- and *l*-Camphoric acid	Acid.
d- and *l*-Camphoric anhydride	Anhydride.
d- and *l*-*ortho*-Methyl hydrogen camphorate	Acid ester.
d- and *l*-Bornyl hydrogen phthalate	Acid ester.
d- and *l*-Pinene	Hydrocarbon.
d- and *l*-Camphene	Hydrocarbon.

If substances are arranged in increasing order of associating power, a sequence is obtained somewhat as follows: Hydrocarbons, anhydrides, ketones, alcohols, acid esters, and acids.

Group 1. The mixed-crystal type of curve is by far the commonest, and in this investigation is given by a hydrocarbon (camphene), a ketone (camphor), an alcohol (borneol), an anhydride, and an acid ester (bornyl hydrogen phthalate). In the case of the acid ester here included, the part conferring optical activity is not in the acidic part of the molecule. The hydrocarbon, anhydride, and ketone which fall into this group show no evidence of association of the pure isomerides and, as the temperatures of melting are all comparatively high, the mixed-crystal type of curve might be expected in place of the curve denoting a simple mixture. With borneol there is evidence of a slight amount of association, and so it might be expected that the racemic compound, if formed, would be largely dissociated. This type of curve is shown by substances which have little or no associating power in the pure isomeride.

Group 2. Pinene and camphene give different types of melting-point curve. The type for pinene is that of the *dl*-conglomerate, a simple mixture of *d*- and *l*-pinene, with no evidence of a racemic compound. The curve for camphene is that of the mixed-crystal type. Both substances, by cryoscopic determinations in benzene, give normal molecular weights. The only striking difference between the two substances is that of the temperatures at which they melt. In general, a rise of temperature favours the formation of mixed crystals, so it is not surprising that, when such similar substances as optical isomerides are being dealt with, the *d*-form should be able to replace the *l*-form without altering the shape of the crystal or its melting point. The fact that so many mixed-crystal types of curves are found for optical isomerides, and that only one, *viz.*, pinene, yields a simple *dl*-conglomerate, points to the conclusion that in many cases where a simple mixture curve might be expected, a mixed-crystal curve is actually obtained.

Group 3. This type exhibits the definite formation of a racemic compound. It includes the two substances which might be expected to give one, since they belong to groups of substances which generally form associated molecules. By calculation, it is shown that the racemic compound formed is only dissociated to a small extent, and so, at the temperature of melting, the racemic compound is present to a large extent in the liquid state. In both cases the theoretical curves agree well with the experimental curves, especially as regards the percentage of eutectic compound, and the discrepancy in the eutectic temperature may be accounted for by considering the heats of dilution and dissociation, which had not

been taken into account in drawing the curve, as no exact values for them could be obtained. The strongly associating substances, then, show distinct evidence of formation of racemic compounds, and furnish curves in group 3; whilst substances of feebly associating power furnish curves in group 1, where the formation of a racemic compound is possible; and substances which show no associating power may be found in group 2, where no racemic compound is possible, or in group 1, where its absence is very probable. Since both associating power and the percentage dissociation of a racemic compound may vary continuously, the one type of curve might be expected to merge into the other. The larger the percentage dissociation of the racemic compound, the more will the type of group 3 approximate to that of group 1. A general review of the position with regard to racemates and pseudo-racemates was given by Landrieu (*Bull. Soc. chim.*, 1922, **31**, 1234). He advanced the view that if the *d*- and *l*-isomerides could form ions, as in the case of acids and salts, they should also tend to form racemic compounds. If, on the other hand, they were non-dissociable, they should form mixed crystals. This conclusion is in agreement with the results of this investigation. Since polar substances are those which give associated compounds, they are also those which give racemic compounds. The fundamental reasons for the formation of racemic compounds are no better understood than those for the formation of associated substances, and it may be that electrical forces are the main factors in both.

Experimental.

Preparation of Optical Isomerides.—Special care was taken to obtain the *d*- and *l*-forms in as pure a state as possible. A Schmidt and Haensch instrument was used in all polarimetric measurements, and all temperatures were corrected for emergent stem, and comparisons made with a standard thermometer.

l-Borneol was obtained from the British Drug Houses, Ltd. After one recrystallisation from light petroleum, it melted at 207° and had $[\alpha]_D^{15°}$ −36·52° in toluene ($c = 11·5$). A second sample gave $[\alpha]_D^{19°}$ −36·81°. This was not sufficiently pure for our purpose, and so a lengthy purification was carried out. The general method is due to Haller (*Compt. rend.*, 1889, **108**, 456). The final product melted at 207·2° and had $[\alpha]_D^{15°}$ −37·50° in toluene ($c = 8$). The second sample gave $[\alpha]_D^{19°}$ −37·65°. This purified substance was used in the determination of the melting-point curves of *d*- and *l*-borneols and also in the preparation of *l*-camphor, *l*-camphoric acid, *l*-camphoric anhydride, and *ortho*-methyl hydrogen *l*-camphorate.

d-Borneol was obtained from the same firm. After one recrystal-

lisation from light petroleum, it melted at 206° and had $[\alpha]_D^{14.5°}$ +29·88° in toluene ($c = 8$). Haller gives $[\alpha]_D$ +37·77°. The correct melting point and the appearance of the crystals seemed to indicate a pure product. The low rotation is due to the fact that commercial *d*-borneol consists of mixed crystals of *d*-borneol and *l-iso*borneol. This was pointed out by McKenzie (J., 1907, **91**, 1225), but the circumstance that Lowry (J., 1925, **127**, 614) employs for accurate polarimetric measurements *d*-borneol of low rotation indicates that this fact is not generally known. After treatment with zinc chloride and further purification as in the case of *l*-borneol, the final product melted at 206·5° and had $[\alpha]_D^{16°}$ +37·1° in toluene ($c = 8$).

l-Camphor was obtained from *l*-borneol, prepared as above, by oxidising it with concentrated nitric acid (Aschan, *Acta Sci. Fennicæ*, 1895, **21**, No. 5) and recrystallising the product from benzene. It melted at 177·7° and had $[\alpha]_D^{16°}$ − 43·61° in absolute alcohol ($c = 16·51$). Beckmann (*Annalen*, 1889, **250**, 253) gives $[\alpha]_D^{16°}$ −44·22°.

d-Camphor was obtained from the commercial product Camphor Ang. After recrystallisation from alcohol, it melted at 178·6° and had $[\alpha]_D^{16°}$ + 44·20° in absolute alcohol ($c = 16·51$). Beckmann gives $[\alpha]_D^{16°}$ +44·22°. This sample was employed in all the experiments without further purification.

l-Camphoric acid was prepared from *l*-borneol by heating it with concentrated nitric acid. After extensive purification, the final product melted at 187·5° and gave $[\alpha]_D^{16°}$ − 48·12° in absolute alcohol ($c = 8·24$).

d-Camphoric acid was obtained from the British Drug Houses, Ltd. After one recrystallisation from aqueous alcohol, it melted at 177—178° and gave $[\alpha]_D^{16°}$ + 47·15° in absolute alcohol ($c = 8·24$). After purification, it had m. p. 187·6° and $[\alpha]_D^{15°}$ +47·6°. From camphoric anhydride, a *d*-acid was obtained of m. p. 188·2° and $[\alpha]_D^{17°}$ +47·75°.

ortho-Methyl hydrogen *l*-camphorate was prepared (*a*) by acting on *l*-camphoric anhydride with sodium methoxide (Walker, J., 1892, **61**, 1088), (*b*) by passing dry hydrogen chloride into a solution of *l*-camphoric acid in methyl alcohol. The oil thus obtained crystallised after some months and thereafter crystallisation could be easily induced by "seeding." After several recrystallisations from light petroleum, the ester melted at 73·5° and gave $[\alpha]_D^{15°}$ − 52·95° in absolute alcohol ($c = 10$) (1 g. required 12·40 c.c. of 0·0371*N*-baryta. Calc.: 12·58 c.c.).

ortho-Methyl hydrogen *d*-camphorate was prepared similarly. It had m. p. 76° and $[\alpha]_D^{15°}$ + 51·95° in absolute alcohol ($c = 10$). Haller (*Compt. rend.*, 1892, **114**, 1516) gives m. p. 75—76° and $[\alpha]_D$ + 51·52°. Titration with baryta showed that the oil and the

crystals had the same composition, and coincided with the theoretical value.

The *l*- and *d*-forms of bornyl hydrogen phthalate were prepared in the course of purification of *l*- and *d*-borneols, and were utilised after one recrystallisation from their respective solvents, benzene and glacial acetic acid.

Pinene gives an optical rotation which seems to depend on its source. It was purified by repeated distillation in steam (a little carbonate being added to the pinene before starting), followed by drying and careful fractionation. The sample of *l*-pinene used was obtained from the British Drug Houses, Ltd.; it had $[\alpha]_D$ — 35·23° and *d* 0·8682. After purification, the main fraction boiled at 160°, had $[\alpha]_D$ — 37·58° and *d* 0·8674, and melted sharply at — 63°. *d*-Pinene was obtained from Kahlbaum: $[\alpha]_D$ + 45·38°, *d* 0·8665. After purification, the main portion had b. p. 156°, $[\alpha]_D$ + 46·80°, and *d* 0·8590, and melted sharply at — 64°.

l-Camphene was obtained from purified *l*-pinene by converting it into pinene hydrochloride and heating this with potassium phenoxide. After fractionation, pure *l*-camphene was obtained, b. p. 160·5°, m. p. 44°, $[\alpha]_D^{15°}$ — 77·15° in absolute alcohol ($c = 10$).

d-Camphene was prepared from purified *d*-pinene in a similar way. It had b. p. 160°, m. p. 46°, and $[\alpha]_D^{15°}$ + 72·8° in absolute alcohol ($c = 11·7$).

As in the case of the pinenes, the rotation seems to depend on the source of the material.

Determination of Curves.

Temperatures were determined by means of thermo-couples, since they allowed of equally accurate determinations over the whole of the range (— 125° to +230°) and required the use of only small quantities of material. The two wires of the thermo-couple (copper–constantan) were sealed through two side-tubes attached to a wider tube ($\frac{1}{2}$ in. diam.), on one end of which a bulb had been blown, and were arranged so that the junction occupied the foot of the bulb. A glass stopper was ground into the other end of the wider tube, so that the determinations could be carried out without loss, some of the substances having a high vapour pressure. In dealing with substances which were volatile at their melting point, stirring was accomplished by an electro-magnetic arrangement (type *a*), and in other cases a glass rod was used as stirrer and worked by hand (type *b*). A sensitive mirror galvanometer was employed, giving an accuracy of 1×10^{-5} volt. The relationship between the ***E.M.F.*** of the thermo-couple and the difference of temperature between the two junctions is not linear, but for small ranges of temperature the

error in regarding it as such is negligible. In general, therefore, for each curve two substances were chosen which melted at steady temperatures, one at each end of the range, and their melting points were found with each thermo-couple and with an accurate thermometer. The following table gives details of the various experiments.

Substances.	Substances used for calibration.	Table and fig.	Remarks.
d- and *l*-Borneol.	Borneol (m. p. 206·5°). Camphor (m. p. 178·6°).	I, 1.	Setting point. Each mixture weighed out separately.
d- and *l*-Camphor.	Same as above.	II, 1.	Same as above.
d-Borneol and *d*-camphor.	,, ,,	III, 2.	Curve already determined by Vanstone (J., 1909, **95**, 597) with impure *d*-borneol.
d- and *l*-Camphoric acid.	,, ,,	IV, 3.	Melting point. The melted acid readily decomposed.
d- and *r*-Camphoric acid.	,, ,,	V, 4.	Melting point. The *r*-acid was prepared by recrystallising equal quantities of the *d*- and *l*-acids from aqueous alcohol.
d- and *l*-Camphoric anhydride.	Camphoric acid (m. p. 223·8°). Borneol (m. p. 206·5°).	VI, 1.	Setting point. No decomposition of melted anhydride.
d- and *l-ortho*-Methyl hydrogen camphorate.	*m*-Dinitrobenzene (m. p. 90·5°). Diphenyl (m. p. 68·7°).	VII, 5.	Melting point. Substance tended to form an oil. Successive quantities of one isomeride added to the mixture in the tube.
d- and *r-ortho*-Methyl hydrogen camphorate.	Same as above.	VIII, 4.	Same as above.
d- and *l*-Bornyl hydrogen phthalate.	Bornyl hydrogen phthalate (m. p. 161·4°). Camphor (m. p. 178·6°).	IX, 1.	Melting point. The melted substance decomposed readily.
d- and *l*-Pinene.	Diethylaniline (m. p. −38·1°). Chloroform (m. p. −63·3°). Toluene (m. p. −94·5°). Ethyl alcohol (m. p. −114·2°).	X, 6.	Melting point.
d- and *l*-Camphene.	Urethane (m. p. 47·8°). Salol (m. p. 41·6°).	XI, 1.	Setting point. No decomposition of melted substance.

Stirrers of type *a* were used in all cases except Nos. VII, VIII, and X, in which type *b* was used.

A glycerol bath was used in all cases except Nos. VII, X, and XI, in which water, liquid air, and water, respectively, were used.

TABLE I.

% *d*-Borneol.	S. p.*
100·0	206·5°
81·3	206·4
72·0	206·6
49·5	206·4
40·8	206·0
35·4	206·2
24·1	206·2
12·4	206·1
10·5	206·8
0·0	207·2

TABLE II.

% *d*-Camphor.	S. p.
100·0	178·6°
86·2	178·8
81·0	178·6
70·8	179·1
57·9	178·7
48·7	178·6
30·1	178·3
19·1	177·8
11·3	178·5
0·0	177·7

TABLE III.

% *d*-Borneol.	S. p.
100·0	206·5°
90·4	201·7
75·7	198·5
57·3	196·2
49·0	192·7
37·8	188·9
21·3	185·3
8·4	181·4
0·0	178·6

TABLE IV.

% *d*-Acid.	M. p.
100·0	187·6°
95·4	185·9
93·5	185·4
92·7	185·9
92·1	185·0
87·3	186·5
74·4	191·3
56·9	197·2
49·8	199·5
47·9	199·6
40·7	196·9
34·4	193·4
28·1	193·3
13·4	187·3
8·9	186·7
5·5	186·8
0·0	187·5

TABLE V.

% *d*-Acid.	M. p.
100·0	188·2°
93·5	187·3
85·4	186·4
81·7	187·2
69·4	189·3
49·2	193·1
36·4	197·1
23·6	198·1
16·0	200·5
0·0	202·6

TABLE VI.

% *d*-Anhydride.	S. p.
100·0	223·8°
88·8	223·5
71·6	222·8
50·2	222·9
41·4	222·2
25·0	221·6
22·1	221·9
9·4	221·7
0·0	222·9

TABLE VII.

% *d*-Ester.	M. p.
100·0	74·3°
95·6	70·8
89·7	66·5
88·0	65·9
87·4	66·2
82·2	66·9
69·5	70·3
53·9	83·6
49·9	84·6
45·7	83·4
38·4	79·1
30·7	70·4
25·8	66·5
17·0	65·0
13·4	64·7
12·0	64·6
9·4	65·0
4·8	67·1
0·0	73·5

TABLE VIII.

% *d*-Ester.	M. p.
100·0	74·4°
90·3	70·5
85·1	68·7
73·1	65·6
60·2	67·6
41·3	74·8
26·0	82·2
9·9	85·5
0·0	85·9

TABLE IX.

% *d*-Phthalate.	M. p.
100·0	161·4°
91·6	160·8
78·9	160·5
60·0	160·9
49·7	161·1
48·1	162·5
38·6	162·5
27·0	162·1
9·7	161·7
5·3	162·3
0·0	162·8

TABLE X.

% *d*-Pinene.	M. p.
100·0	− 64·1°
84·5	− 72·5
75·8	− 77·7
63·6	− 98·1
56·6	−113·8
54·0	−115·1
50·7	−120·2
48·5	−115·4
42·3	−109·5
28·9	− 79·6
20·1	− 76·7
16·9	− 72·2
9·4	− 68·0
0·0	− 63·1

TABLE XI.

% *d*-Camphene.	S. p.
100·0	46·5°
77·2	46·0
60·6	45·4
52·9	45·0
48·0	44·8
41·6	44·6
29·8	44·2
20·7	43·9
0·0	43·7

* S. p. indicates setting point.

Analysis of Experimental Curves.

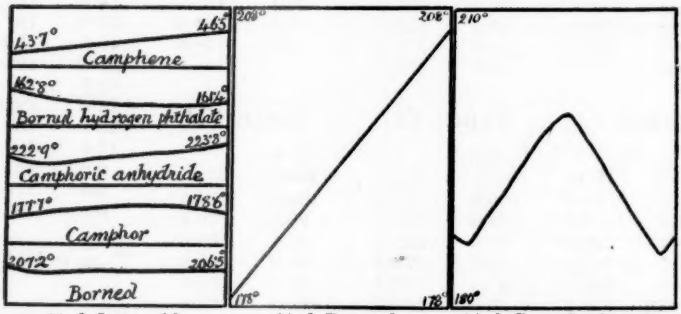
The curves obtained fall into the three classes described by Roozeboom (p. 2770).

In class (1) are most of the substances investigated, *viz.*, borneol, camphor, camphoric anhydride, bornyl hydrogen phthalate, and camphene. In class (2) is the curve for *d*- and *l*-pinene, and it is

the only curve of this kind that has yet been obtained for two optical isomerides. In class (3) are camphoric acid and *ortho*-methyl hydrogen camphorate.

The curves of class (1) do not lend themselves to exact mathematical examination. The equation which they follow has been worked out by van Laar (*Z. physikal. Chem.*, 1908, **64**, 289) and is,

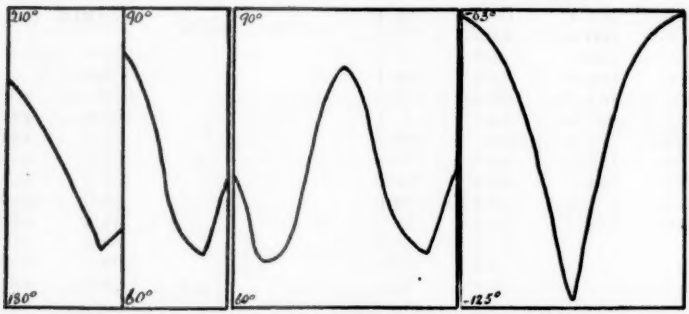
FIG. 1. FIG. 2. FIG. 3.



% d-*Isomeride.* % d-*Borneol.* % d-*Camphoric acid.*

of course, of the simple form $T = T_0 =$ constant, *i.e.*, the curve should be a straight line joining the melting points of the pure *d*- and *l*-isomerides, and should be at right angles to the temperature axis. All the curves found have this general form. Since the *d*- and *l*-isomerides may form mixed crystals with each other, and the

FIG. 4. FIG. 5. FIG. 6.

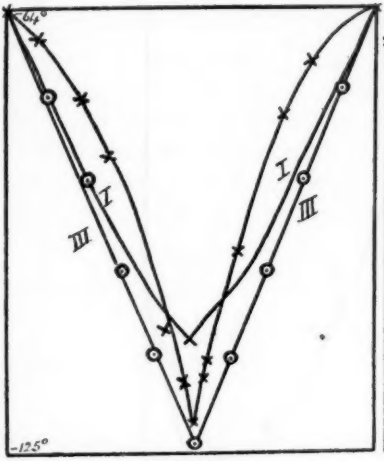


% d-*Acid.* % d-*Ester* % d-*Ester.* % d-*Pinene.*

racemate, if formed, may also give mixed crystals with the *d*- and *l*-isomerides, it is evident that this type of melting-point curve does not give a definite answer to the question as to whether a racemic compound is formed or not. Tammann has investigated this question (*Z. physikal. Chem.*, 1914, **87**, 357) and, by calculating the value of the quotient of the latent heat and the absolute tem-

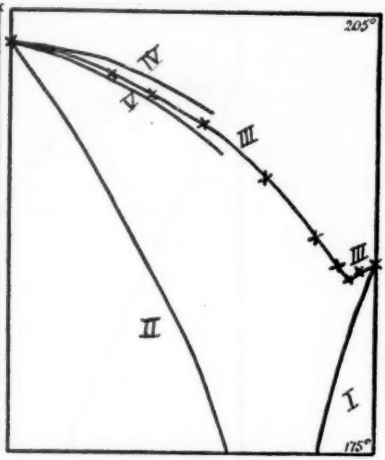
perature of melting, *i.e.*, l_a/T_{0a} for the pure isomerides, and for their 50% mixture, he obtains evidence as to whether he is dealing with a racemate or a pseudo-racemate. The assumption on which

FIG. 7.



% d-*Pinene*.

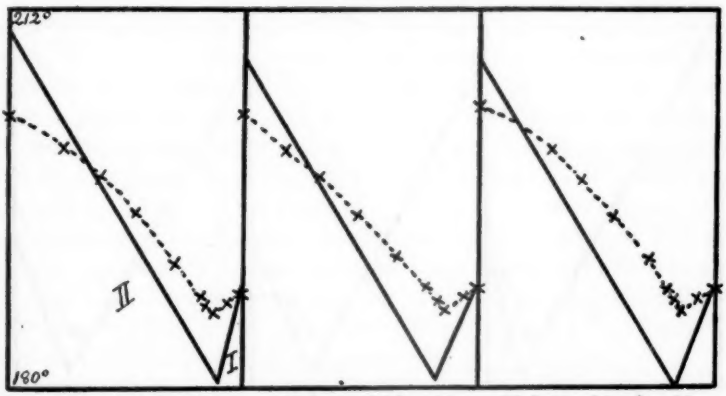
FIG. 8.



Mol. % *of* d-*acid*.

this is based is that the pure *d*- and *l*-isomerides consist of simple molecules. The same criterion, which Tammann takes as evidence of the formation of a racemate, may be applied to the pure *d*- or

FIG. 9.

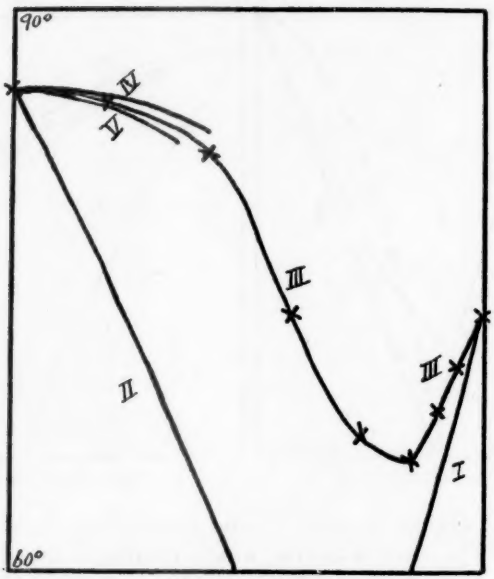


Mol. % *of* d-*acid*. *Mol.* % *of* 2d-*acid*. *Mol.* % *of* 1·8d-*acid*.

l-isomerides to determine whether or not they are associated. In the case of the pure isomerides, the formula becomes Trouton's rule, as modified by Walden to apply to melting points. It is evident,

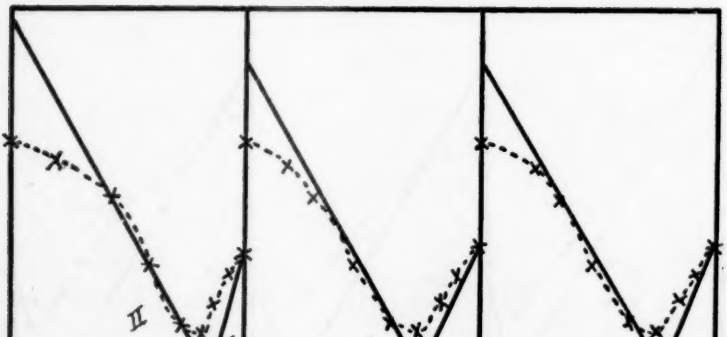
then, that if the *d*-isomeride is associated to the same extent with itself as it is with the *l*-isomeride in the racemic compound, the same value of the ratio l/T should be obtained for the pure

FIG. 10.



Mol. % of d-*ester.*

FIG. 11.



Mol. % of d-*ester.* *Mol. % of* 2d-*ester.* *Mol. % of* 1·7d-*ester.*

d-isomeride and for the 50% mixture with the *l*-isomeride. This is the criterion which Tammann uses to establish the absence of a racemic compound.

Before the mathematical analysis of the curves of types (2) and (3) is discussed, the equations which apply to substances at their melting points may be considered generally. The ordinary law for the lowering of the melting point of a pure substance A by the addition of another pure substance B may be written as

$$dT/dx_a = RT^2/L_a \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where T is the melting point on the absolute scale, R the gas constant, L_a the latent heat of the substance A per g.-mol., and x_a the molar fraction of the substance A.

Washburn and Read (*loc. cit.*) suggest that for the exact analysis of the melting-point curves of the two substances A and B we should use, instead of the formula of van 't Hoff, the expressions

$$dT/dx_a = RT^2/L_a x_a \text{ and } dT/dx_b = RT^2/L_b x_b \quad . \quad . \quad (2)$$

On integrating equation (1) we get

$$x_b = 1 - x_a = (1/T - 1/T_{0a})L_a/R$$

and from equation (2) we get

$$\log_e x_a = (1/T_{0a} - 1/T)L_a/R.$$

These two equations are the same for small values of x_b.

The values for the latent heats of the substances used were calculated from the values of the molecular depression, k. If $K = 100k$, and M is the molecular weight of the substance, Raoult's freezing-point law gives the third equation

$$dT/dx_a = K/M \quad . \quad . \quad . \quad . \quad . \quad (3)$$

d- *and* l-*Pinenes.*—The values of the melting points were calculated according to the equations (1), (2), and (3). The curves are shown in Fig. 7: curve I is calculated from equation (1); curve III from equation (3); circles ⊙ represent equation (2); and the experimental points are indicated by crosses. All the curves intersect at the 50% mixture, but the value for the eutectic temperature is slightly lower than the experimental value in the case of the straight-line curve. The value given by the van 't Hoff equation is considerably higher than the experimental value. There is no doubt that in the case of *d*- and *l*-pinenes we are dealing with a simple mixture of two substances, and the curve approximates closely to that given by an "ideal" solution. The value of K was found by determination of the molecular depression to be 16500.

d- *and* r-*Camphoric Acids.*—In this case the curves have to be considered in two sections: (1) *d*-acid in presence of *r*-acid, and (2) *l*-acid in presence of *r*-acid. For the *d*-acid, $K = 17500$ and $L = 4835$; and for the *r*-acid, $K = 13000$ and $L = 13840$. The curves corresponding to equation (1) are shown in Fig. 8, I and II.

In the same figure the experimental values are indicated by crosses. It is evident that the course of the curve calculated from equation (1) does not follow the experimental curve.

The shape of the curve near the melting point of the *r*-acid indicates the degree to which the acid is dissociated into its components. Kremann (*loc. cit.*) has shown how the shape of the curve may be found, if definite percentages of dissociation of the compound are assumed (compare Findlay and Hickmans, *loc. cit.*). On the assumption of 10% and 15% dissociation the following values for the melting points corresponding to different fractions of *d*-acid added were obtained.

x	0·0	0·2	0·4
t for 10%	202·6°	201·0°	198·3°
t for 15%	202·6	201·9	199·7

The curves IV and V were drawn in Fig. 8 corresponding to 15% and 10% dissociation, respectively; and the experimental curve was found to lie between them. The degree of dissociation of the *r*-acid being assumed to be 12%, its calculated melting point would be 209·6° if there were no dissociation. Taking this value for the melting point of the pure *r*-acid, we have drawn the straight line with $dT/dx = 32{\cdot}5$, and that with $dT/dx = 87{\cdot}5$ for the *d*-acid (Fig. 9, curves I and II). These two straight lines give the percentage of the eutectic mixture fairly accurately, but not the eutectic temperature. The curves were again drawn on the assumption that we were dealing with *r*-acid and 2*d*-acid. The melting point of the pure racemic acid would now be 206·5° if we assume it to be dissociated into 2*d*- and 2*l*-acids to the extent of 12% (Fig. 9). Thirdly, the curve was drawn on the assumption that the *d*-acid was associated to the same extent as it is associated with the *l*-acid in the racemic compound, so that the average size of the *d*-molecule is 1·8*d*. The melting point of the pure racemic acid would be 206·8° if we assume it to be dissociated into 1·8*d*- and 1·8*l*-acids to the extent of 12%. The curves are shown in Fig. 9.

All three curves give the eutectic percentage about equally well, but not the eutectic temperature accurately. It is obvious that no assumption with regard to the molecular complexity of the *d*- and *l*-acid will give two straight lines intersecting both at the eutectic temperature and at the eutectic percentage. The reason for this may be that in calculating the gradient we have taken into account only the latent heat of fusion, and not the possible heat of dilution of *d*- and *r*-acid, or the heat of dissociation of those acids. Van Laar has worked out a formula for α, the degree of dissociation of a compound, in terms of known values. Kremann found that the values given by this formula were about twice as large as those

given by the graphical method. Calculating α for racemic acid, we get

$$\alpha = \frac{RT^2}{L} \cdot \frac{x^2(1+x)}{4(T_0 - T)} = \frac{K}{M} \cdot \frac{x^2(1+x)}{4(T_0 - T)} = \frac{13000}{400} \cdot \frac{0{\cdot}04 \times 1{\cdot}2}{4 \times 1{\cdot}2} = 0{\cdot}32.$$

The value for the degree of dissociation given by this formula is nearly 2·5 times as great as that given by the graphical method. This value would, of course, be reduced if we took into account the possible heat of dilution and the heat of dissociation. Evidence for the molecular complexity of camphoric acid is somewhat difficult to obtain, since it is not sufficiently soluble for a molecular weight determination to be made in benzene. In alcohol the molecular weight is rather less than normal, but that is not a surprising result, since alcohol generally gives low results even with associated substances. The general behaviour of organic acids would show that as a class they are associated.

d- *and* r-*Methyl Hydrogen Camphorates.*—The curves obtained for the esters may be considered in the same way as those for the acids. For the *d*-ester, $K = 23000$ and $L = 2234$, whilst for the *r*-ester, $K = 18800$ and $L = 5838$. The curves corresponding to equation (1) are shown in Fig. 10, I and II, and experimental values are indicated by crosses. Again the curve drawn according to equation (1) does not follow the experimental curve.

By a similar calculation to that employed in the case of camphoric acid, we can draw curves for the various percentages of dissociation of the *r*-compound. Assuming 20% and 15% dissociation, the following values of the melting points corresponding to different fractions of *d*-ester added were obtained.

x	0·0	0·2	0·4
t for 15%	85·9°	84·9°	82·0°
t for 20%	85·9	85·4	83·4

The curves IV and V were drawn in Fig. 10 corresponding to 20% and 15% dissociation, respectively, and the experimental curve was found to lie between them. The degree of dissociation of the *r*-ester was taken as 18%. Taking $dT/dX = 43{\cdot}9$ for the *r*-ester, and $dT/dx = 107{\cdot}5$ for the *d*-ester, the curves in Fig. 11 were drawn as in the case of the acid. In the case of the ester the curves for 2*d*- and 1·7*d*-ester give very good agreement for the eutectic percentage, and the eutectic temperature is not so much below the experimental value as in the case of the acid. It is probable, therefore, that the heat of dilution and the heat of dissociation are not so large as in the case of the acid. Calculating α, the degree of dissociation of the *r*-ester, in terms of van Laar's formula we get

$$\alpha = \frac{18800}{428} \times \frac{0{\cdot}04 \times 1{\cdot}2}{4 \times 0{\cdot}75} = 0{\cdot}70.$$

This is nearly 3·5 times as great as the value given by the graphical method. An ebullioscopic determination in benzene gave M, 325; there is thus a considerable amount of association. The values of the melting points of the ester mixtures are more trustworthy than those found for the acid, because there was no sign of decomposition in the case of the melted ester. The only difficulty was that the ester tended to remain as an oil for a long time so that calorimetric determinations of the heat data were not obtainable.

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CCCLXVII.—*The Systems Sodium Iodide–Acetone and Sodium Iodide–Methyl Ethyl Ketone.*

By ALAN ERIC WADSWORTH and HARRY MEDFORTH DAWSON.

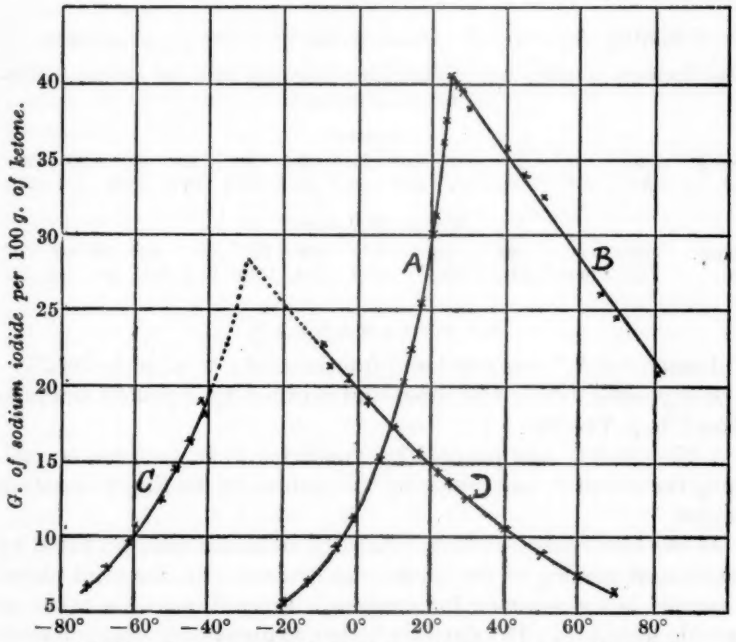
IN connexion with the purification of acetone for use in experiments on the reaction between acetone and iodine, the authors were led to inquire into the relations underlying the sodium iodide method described by Shipsey and Werner (J., 1913, **103**, 1255). The inquiry was subsequently extended to ascertain whether the same method could be used for the purification of methyl ethyl ketone. Although the experiments with the latter are not as complete as it was hoped to make them, it seems desirable to place our results on record, more particularly since observations on the system sodium iodide–acetone have just been published by Macy and Thomas (*J. Amer. Chem. Soc.*, 1926, **48**, 1547).

In general, our results for acetone are in agreement with those of Macy and Thomas. At low temperatures the stable solid phase is the compound $NaI,3CMe_2O$, which is converted into the simple iodide at 25·7°. The solubility of the acetone salt complex increases rapidly with rise of temperature, whereas the simple salt shows a rapid fall.

Corresponding measurements with sodium iodide and methyl ethyl ketone show that this system is very similar to the acetone system. Between — 75° and — 45°, the concentration of the sodium iodide in the liquid phase increases rapidly with rise of

temperature, whilst between — 10° and + 70° the proportion of sodium iodide in the saturated solution shows a rapid fall. Over the higher range of temperature, the solid phase is the simple iodide, and the close similarity between the curve systems for the two different ketones suggests that the complex NaI,3COMeEt is the solid phase at lower temperatures. The point at which this complex is transformed into the simple salt is apparently not far removed from — 30°.

FIG. 1.



Solubility of sodium iodide in acetone (curves A *and* B*) and in methyl ethyl ketone (curves* C *and* D*).*

The observations made with methyl ethyl ketone indicate that this also may be purified by the use of sodium iodide. The conditions necessary for such purification are, however, radically different from those prescribed by Lochte (*Ind. Eng. Chem.*, 1924, **16**, 956), whose method consists in boiling the moist ketone with excess of sodium iodide, filtering the saturated solution, and allowing it to crystallise at the ordinary temperature. The fact that no result was obtained by Lochte when dry sodium iodide and dry ketone were used is quite in harmony with our observations. The fact that a maximum yield of crystals was obtained by him when the water present was just sufficient to form sodium iodide dihydrate

suggests, however, that the crystalline substance which separates out in the procedure recommended by Lochte is hydrated sodium iodide, and it is clear that his method cannot possibly lead to the desired result.

The conditions actually required for the successful and economic purification of methyl ethyl ketone and of acetone can be deduced from the respective solubility curves shown in the diagram, and need not be further discussed. Solubility data taken from the smooth curves are given below for even temperatures.

Solubility Data (*g. of sodium iodide per* 100 *g. of solvent*).

(The numbers in italics refer to solutions saturated with the sodium iodide–ketone complex.)

Acetone.

Temp.	−20°	−10°	0°	10°	20°	25·7°	30°	40°	50°	60°	70°	80°
Sol.	*5·5*	*7·8*	*11·8*	*18·2*	*30·0*	40·7	39·2	35·6	32·0	28·6	25·1	21·8

Methyl ethyl ketone.

Temp.	−70°	−60°	−50°	−10°	0°	10°	20°	30°	40°	50°	60°	70°
Sol.	*7·3*	*10·0*	*14·0*	22·8	20·1	17·4	15·0	12·7	10·7	8·9	7·4	6·2

EXPERIMENTAL.

Acetone "*A.R.*" was dried and fractionated; b. p. 56·1—56·2°.

Methyl ethyl ketone was dried and purified by repeated fractionation; b. p. 78—79°.

Sodium iodide was purified by dissolving it in acetone, crystallising the complex, and removing the acetone by heating to constant weight.

At the lower temperatures, saturated solutions were prepared by mechanical stirring of the solution in contact with the solid phase, a sample being removed for analysis. Precautions were taken to exclude moisture. The data for higher temperatures were obtained by enclosing weighed quantities of sodium iodide and ketone in sealed tubes, the contents of which were effectively shaken while the temperature was very slowly raised or lowered. The temperatures at which the solid phase just disappeared on cooling, or made its appearance on warming, agreed closely, usually within 0·1°. In other words, there was little tendency towards formation of supersaturated solutions. In the experiments at the highest temperatures, the vapour space was kept as small as possible, and the requisite small correction applied to obtain the amount of solvent actually in the liquid state.

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CCCLXVIII.—*The Influence of Dissolved Salts on the Mutual Miscibility Temperature of the Systems Ethyl Alcohol or Methyl Alcohol–Paraffins.*

By Edward John Howard and William Hamilton Patterson.

The change of critical solution temperature (C.S.T.) of the system water–phenol caused by the addition of various salts has been described (Carrington, Hickson, and Patterson, J., 1925, **127**, 2544). For the systems described below, with ethyl or methyl alcohol as the salt solvent, some modification was necessary in procedure.

System 1. *Ethyl Alcohol–Paraffin.*—The paraffin was a fraction of b. p. 160—180°. The alcohol was obtained by purifying and dehydrating 99·5% alcohol. The critical mixture (C.S.T. 33·5°) contained only 13% of alcohol. Instead of this a 50% mixture (by weight) was used in all cases. This mixture, the mutual miscibility temperature (M.M.T.) of which was 19·9°, was so hygroscopic that a blank M.M.T. was determined in each set of experiments. The highest reference temperature (used in the case of cadmium nitrate only) was 23·3°, representing a water absorption of 0·25%.

System 2. *Methyl Alcohol–Hexane.*—The hexane, b. p. 68—69°, was obtained by fractionally distilling petrol. The alcohol was shown to be practically water-free by means of Rothmund's solubility curve (*Z. physikal. Chem.*, 1898, **26**, 433). The critical mixture (C.S.T. 42·0°) contained 20% of methyl alcohol and was too deficient in this component for convenient observation. The mixture used contained 50% of each component by weight and had an initial M.M.T. of 35·5°. Blank determinations were made as before in each set of experiments. The highest M.M.T., 40·5° (used in the case of zinc chloride), represents a water absorption of 0·4%.

All salts were prepared anhydrous. Experiments were carried out in stoppered tubes of thick glass so as to avoid evaporation and water absorption.

The results are stated in the tables in terms of the molecular concentration C, *i.e.*, g.-mols. of salt per 1000 g. of *total alcohol and salt*; e is the elevation of M.M.T.; and $E = e/C$, the molecular elevation of M.M.T. In each case the value of e is shown above that of E. To facilitate comparison of the various systems, concentrations are expressed in terms of the salt solvent only. Values of e and E at even concentrations are obtained by interpolation from

separate curves; a bracketed number indicates slight extrapolation. The values for water, nearly identical in both systems, have been included.

Values of e *and* E.

System 1: *Ethyl alcohol–paraffin.*

Molecular concentrations.

Salt.	0·02.	0·04.	0·06.	0·08.	0·10.	0·12.	0·16.	0·20.	0·24.
LiI	5·25°	8·1°	10·6°	13·05°	15·5°	17·85°	22·5°	27·1°	—
	255°	197°	175°	163°	154°	148°	139°	136°	(134°)
NaI	5·0	7·65	9·9	12·1	14·3	16·4	20·6	24·7	(28·7)
	225	187	165	151	142	136	129	123	(120)
NH_4I	4·2	6·8	9·3	11·5	13·6	15·65	19·55	23·25	(27·0)
	206	175	155	144	136	130	122	115	(113)
KI	(3·65)	5·65	7·5	9·4	11·25	(13·15)	—	—	—
	—	140	125	118	113	110	—	—	—
LiBr	(4·35)	6·95	9·3	11·4	13·5	15·5	19·5	23·4	(27·3)
	(215)	180	156	144	135	129	122	117	(114)
NaBr	4·0	6·5	8·45	10·25	12·1	13·9	17·5	21·0	—
	184	160	142	131	122	116	110	105	(102)
NH_4Br	(4·0)	6·45	8·4	10·2	12·0	13·65	16·75	19·7	(22·7)
	—	160	140	127	120	115	107	100	(94·5)
$LiNO_3$	(4·0)	6·6	8·75	10·8	12·75	14·55	18·0	21·45	24·9
	—	164	146	135	126	120	112	108	104
LiCl	(4·0)	6·5	8·45	10·25	12·1	13·9	17·3	20·4	23·45
	—	159	142	131	122	116	108	102	97·5
$CH_3{\cdot}CO_2Na$	(1·5)	(2·75)	3·95	5·0	5·8	6·25	7·15	8·1	9·0
	—	(68·8)	65·6	64·0	59·0	53·0	44·8	40·2	37·2

	0·02.	0·06.	0·10.	0·16.	0·24.	0·30.	0·40.	0·50.	0·60.
$FeCl_3$	(2·8)	6·5°	10·05°	15·3°	22·1°	26·95°	—	—	—
	—	107°	101°	96·0°	92·0°	89·9	—	—	—
$FeCl_2$	(2·0)	4·4	6·7	9·95	—	—	—	—	—
	—	74·0	68·0	62·0	—	—	—	—	—
$CoCl_2$	(1·85)	4·8	7·35	10·95	15·55	18·9	(24·5)	—	—
	—	78·5	73·5	68·8	64·9	62·7	61·2	—	—
$NiCl_2$	(2·1)	4·9	7·3	10·65	15·1	18·45	24·0	(29·55)	—
	—	82·0	73·0	67·2	63·0	61·2	59·8	(59·1)	—
$CaCl_2$	(2·7)	5·3	7·65	11·2	16·1	19·8	26·0	—	—
	—	87·5	76·5	69·8	66·9	65·7	65·1	(65·0)	—
$MgCl_2$	(1·6)	4·1	6·15	9·2	13·15	16·15	(21·15)	—	—
	—	67·5	62·5	57·5	54·2	53·3	(53·0)	—	—
$ZnCl_2$	(1·0)	3·05	5·05	8·2	12·3	15·4	20·6	25·8	—
	(51·5)	51·5	51·5	51·4	51·4	51·4	51·5	51·6	—
$CdCl_2$	1·3	3·25	(5·1)	—	—	—	—	—	—
	70·0	54·2	(51·2)	—	—	—	—	—	—
$CdBr_2$	(1·5)	4·0	6·35	9·8	14·3	17·7	23·65	(29·7)	—
	(70·5)	66·2	63·5	60·8	59·5	59·4	59·2	(59·2)	—
CdI_2	(1·3)	3·6	5·9	9·25	13·4	16·3	21·1	26·0	—
	(63·7)	61·7	60·0	57·7	55·2	53·6	52·2	52·0	(52·0)
$Cd(NO_3)_2$	(2·45)	5·6	8·5	12·75	18·45	22·7	—	—	—
	—	92·0	85·0	79·4	76·8	76·8	—	—	—
$CuCl_2$	(1·1)	3·0	4·45	6·6	9·4	11·55	15·3	19·0	22·8
	—	49·1	45·7	41·6	38·7	38·2	38·0	38·0	38·1
$HgCl_2$	(0·2)	0·7	1·15	1·85	2·8	3·55	4·8	6·05	(7·3)
	—	(11·2)	11·2	11·3	11·4	11·6	11·9	12·2	(12·4)
$HgBr_2$	(0·05)	(0·1)	0·1	0·1	0·1	0·1	0·4	0·9	(1·4)
	—	—	1·7	1·1	0·4	0·5	1·0	1·7	(2·4)
HgI_2	−0·25	−0·75	—	—	—	—	—	—	—
	−12·2	−12·1	(−11·9)	—	—	—	—	—	—
$Hg(CN)_2$	(0·8)	2·5	4·2	6·75	10·15	(12·7)	—	—	—
	(42·2)	42·2	42·2	42·2	42·3	(42·3)	—	—	—
Ca Butyrate	(0·6)	1·65	2·5	—	—	—	—	—	—
	—	27·6	26·0	—	—	—	—	—	—
Ca *iso*Butyrate	(0·4)	1·1	1·65	—	—	—	—	—	—
	—	18·4	16·8	—	—	—	—	—	—
Water	(0·55)	1·55	2·45	3·8	5·5	6·7	8·65	10·65	12·65
	(26·4)	25·3	24·2	23·2	22·5	22·1	21·6	21·2	21·0

System 2 : Methyl alcohol–hexane.

Molecular concentrations.

Salt.	0·02.	0·04.	0·06	0·08.	0·10.	0·12.	0·16.	0·20.	0·24.
NaI	(3·65°)	6·3°	8·6°	10·9°	13·15°	15·4°	19·8°	24·1°	(28·2°)
	—	155°	142°	136°	132°	129°	124°	121°	(117°)
KI	(3·8)	(6·45)	8·85	11·2	13·5	15·7	20·0	(24·1)	—
	—	(158)	147	141	136	131	125	(120)	—
NH_4I	(3·8)	6·45	8·85	11·2	13·5	15·65	19·65	23·5	27·35
	—	161	149	141	136	130	123	118	114
LiBr	(4·0)	6·75	8·9	11·25	13·5	15·7	19·85	23·65	—
	—	167	150	142	137	132	125	119	—
NaBr	(3·65)	6·3	8·6	10·75	12·9	15·0	19·0	22·65	(26·2)
	—	158	144	134	128	125	118	113	(109)
LiCl	(5·2)	(8·5)	11·35	14·2	16·75	19·35	—	—	—
	—	(215)	189	176	168	161	—	—	—
NaCl	4·8	—	—	—	—	—	—	—	—
	242	—	—	—	—	—	—	—	—
$LiNO_3$	(3·45)	(6·0)	8·1	10·1	12·1	14·05	17·8	21·4	25·1
	—	—	135	126	121	117	111	107	104

	0·02.	0·06.	0·10.	0·16.	0·24.	0·30.	0·40.	0·50	0·60.
$FeCl_3$	(2·55°)	6·7°	10·2°	15·15°	21·7°	26·6°	—	—	—
	—	112°	103°	95·0°	90·0°	89·1°	—	—	—
$FeCl_2$	(2·75)	6·9	10·75	16·0	21·9	—	—	—	—
	—	116	109	99·7	91·5	—	—	—	—
$CoCl_2$	(2·95)	6·95	10·5	15·6	21·45	—	—	—	—
	—	115	105	97·2	89·1	—	—	—	—
$NiCl_2$	(2·75)	6·65	10·1	15·0	20·8	—	—	—	—
	—	111	102	94·0	86·9	—	—	—	—
$CaCl_2$	(3·45)	8·2	12·25	18·2	25·95	—	—	—	—
	—	136	122	114	108	—	—	—	—
$MgCl_2$	(3·45)	8·1	12·35	18·7	(27·1)	—	—	—	—
	—	136	123	117	(113)	—	—	—	—
$ZnCl_2$	(1·0)	2·95	4·9	7·9	12·0	15·2	20·55	—	—
	—	50·5	49·9	49·4	49·4	49·9	51·2	—	—
$CdCl_2$	1·85	(4·8)	—	—	—	—	—	—	—
	93·0	(79·0)	—	—	—	—	—	—	—
$CdBr_2$	(1·25)	(3·9)	6·5	10·3	15·45	19·25	25·7	—	—
	—	(65·0)	64·5	64·0	64·0	64·0	64·4	—	—
CdI_2	(1·25)	(3·8)	6·35	10·2	15·35	19·35	26·1	—	—
	—	(63·5)	63·5	63·5	63·5	63·7	(65·0)	—	—
$Cd(NO_3)_2$	(2·5)	(6·9)	11·0	16·8	(24·05)	—	—	—	—
	—	(115)	109	105	(100)	—	—	—	—
$CuCl_2$]	(1·45)	(4·15)	6·6	10·1	14·7	18·2	23·9	—	—
	—	69·0	66·5	63·2	60·8	60·2	59·7	—	—
$HgCl_2$	(0·45)	(1·4)	2·4	3·9	5·9	7·35	9·8	12·3	14·75
	—	(24·5)	24·5	24·5	24·4	24·4	24·5	24·5	24·5
$HgBr_2$	(0·25)	(0·85)	1·4	2·3	3·45	4·35	5·85	7·4	—
	—	(15·7)	15·4	14·8	14·4	14·5	14·7	14·9	—
HgI_2	0·12	0·12	0·12	—	—	—	—	—	—
	6·0	2·0	1·2	—	—	—	—	—	—
$Hg(CN)_2$	(0·9)	(2·8)	4·65	7·45	11·25	14·15	19·15	24·65	—
	—	(47·5)	47·5	47·4	47·4	47·4	47·9	48·7	—
Water	(0·4)	(1·3)	2·15	3·5	5·3	6·55	8·60	10·65	12·7
	—	(22·4)	22·2	22·1	21·9	21·6	21·5	21·3	21·1

Discussion.

Until the results obtained for numerous systems have been correlated it is sufficient to summarise the chief deductions from the behaviour of solutions of salts in ethyl and methyl alcohols. A strict comparison with, *e.g.*, the system water–phenol, cannot be made on account of the temperature differences and of the many salts practically insoluble in alcohol.

(i). The choice of the second liquid of the system (other than the salt solvent) is, *ceteris paribus*, immaterial to the results, provided, of course, that the salts are insoluble in it. Other cases will be

given later (compare the system methyl alcohol–carbon disulphide, Drücker, *Rec. trav. chim.*, 1923, **42**, 552).

(ii). The ions may be arranged in the order of the effects they produce :

System 1. $I > Br > NO_3 > Cl >$ Butyrate $>$ *iso*Butyrate.
$Li > Na > NH_4 > K > Ca > Co = Ni > Fe'' > Mg > Zn = Cd > Cu > Hg''$.

System 2. $Cl > I > Br > NO_3$.
$Li > Na = K = NH_4 > Mg = Ca > Fe'' = Co = Ni > Cd > Cu > Zn > Hg''$.

In system 1 the order of the univalent cations is nearly the same as, and in system 2 it is still nearer, that for aqueous solutions. (In the system water–phenol, lithium as the first member of a group was shown to be out of place in that it was intermediate between sodium and potassium. This is not so, however, at lower temperatures, *e.g.*, in the system water–butyric acid.) The order of the anions in (1) is nearly the reverse of that for aqueous solutions, and in (2) it is intermediate between that for aqueous solutions and that in (1).

(iii). In system 1 the effect of the anions is rather greater, and in system 2 it is much greater, than that of the cations. This applies also to aqueous solutions.

(iv). In system 1 univalent ions, especially cations, produce a greater rise than bivalent or tervalent ions. In system 2 ions carrying one and two charges have nearly the same effect, although the former still predominate. This is in marked contrast to aqueous solutions, where the effect of bivalent ions is double that of univalent.

In general, the magnitude of the effects discussed in (ii), (iii), and (iv) is in the order to be expected from, *e.g.*, the dielectric constants : water, methyl alcohol, ethyl alcohol.

(v). The tests of complexity or association in aqueous solution are applicable to alcoholic solutions.

In cases of normal solution there is a slight change in the variation of e with C (possibly due to change of solvation), which is accentuated in the change (decrease) of E. The lines obtained on plotting log e against log C for alcoholic solutions, however, are not quite straight.

Abnormality is shown by zinc, cadmium, and mercuric halides, mercuric cyanide, and water : in these cases the value of E is remarkably constant. Association is best shown by a comparison of curves ; thus, cadmium halides in each alcohol give very low values compared with those of the alkali halides, contrasted with cadmium nitrate relative to lithium nitrate ; nitrates being assumed to be normal in solution.

Since cadmium iodide gives about half the rise to be expected for the normal molecule, it is probably present in alcoholic solution mainly as Cd_2I_4. The association of the bromide and chloride is correspondingly less. E is constant and often negative when a solute is soluble in both phases (Duckett and Patterson, *J. Physical Chem.*, 1925, **29**, 295). The negative values for mercuric iodide in both alcohols and the very small positive values for the bromide are accounted for by this fact, in addition to molecular association. The solubility of these mercuric salts in hexane and paraffin was verified experimentally. The other salts mentioned were insoluble in the second liquid, so that the low values may well be a measure of the association. The much higher value for mercuric cyanide, in contrast with other mercuric salts, is noteworthy.

In ethyl alcohol, the effect of ferric chloride is much greater than that of ferrous chloride; in methyl alcohol, it is slightly less. Ferric chloride is present in ethyl alcohol probably as $FeCl_3$, and this simple molecule may be partly associated in methyl alcohol.

The curve for sodium acetate has an inflexion at $C = 0{\cdot}10$, indicating some alcoholysis.

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CCCLXIX.—*Miscibility Tests of Dilute Solutions of Chromic Chloride Hexahydrates.*

By JOHN EDWARD HOWARD and WILLIAM HAMILTON PATTERSON.

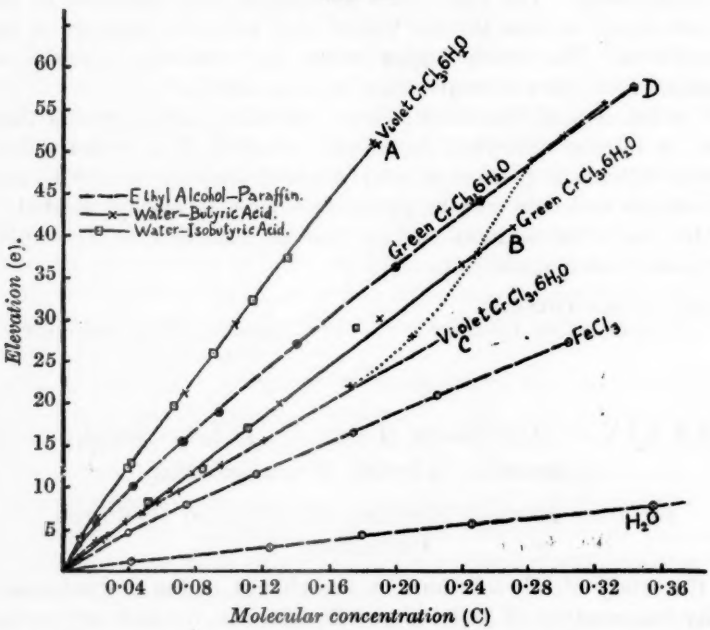
IN the study of salt solutions by the change in the mutual miscibility temperature (M.M.T.) of two liquids, one of which acts as the salt solvent (water and phenol; Carrington, Hickson, and Patterson, J., 1925, **127**, 2544: ethyl and methyl alcohols with paraffins; Howard and Patterson, preceding paper: water with butyric and *iso*butyric acids; Patterson, unpublished research), it was considered advantageous to deal separately with the chromic chloride hexahydrates.

The two isomerides considered are the violet salt, formulated by Werner and Gubser (*Ber.*, 1901, **34**, 1579) as hexa-aquochromic chloride, $[Cr(H_2O)_6]Cl_3$, and the green salt, dihydrated dichlorotetra-aquochromic chloride, $[Cr(H_2O)_4Cl_2]Cl,2H_2O$. These are hereafter referred to by their colours. The intermediate isomeride of this type, first prepared as a solid by Bjerrum (*Ber.*, 1906, **39**, 1597), was not used in making up solutions on account of its

instability. It appears probable, however, that it is present in solutions in equilibrium (compare Fig. 2) and that similar results may be deduced as in the case of the other isomerides.

Various preparations were used and it was shown that the violet solid could be kept in stoppered bottles for several months and still give the same results. Details of preparation and analysis will appear in a subsequent communication by Partington and Tweedy, whom we have to thank for the samples.

FIG. 1.



The liquid pairs used and their critical solution temperatures were:

(1) Water–butyric acid, 26%; C.S.T. −1·2° to 1·05°.
(2) Water–*iso*butyric acid, 30%; C.S.T. 17·50° to 17·95°.
(3) Water–phenol, 36·1%; C.S.T. 66·0°.
(4) Ethyl alcohol–paraffin (b. p. 160—180°), equal parts by weight; M.M.T. 20·0°.

[The range of C.S.T. in (1) and (2) represents a slow change which occurs in aqueous solutions of butyric and *iso*butyric acids during the course of several months, referred to elsewhere.] By use of these liquid pairs it is possible to study the state of salts in solution at temperatures above the respective C.S.T.'s.

In what follows, C is the concentration in g.-mols. of salt per 1000 g. of total aqueous or alcoholic solution (not total mixture), e is the rise in C.S.T. or M.M.T., at the time of the experiment, on dissolving the salt, and $E = e/C$. It has been shown in other cases that it is simpler to calculate concentrations on the salt solvent only; in the present case, in aqueous solution, the same rise is obtained working in butyric or *iso*butyric acid systems (over a temperature interval of 0—55°), indicating little change of hydration. The figures obtained for these systems, therefore, are classified together in the following table, where the values are interpolated for even concentrations, the actual observations being shown in the curves A and B in Fig. 1.

	Systems. Water–butyric acid. Water–*iso*butyric acid.				System. Ethyl alcohol–paraffin.			
	Violet.		Green.		Violet.		Green.	
C.	e.	E.	e.	E.	e.	E.	e.	E.
0·01	3·6°	354°	1·85°	186°	1·9°	—	3·0°	—
0·02	6·4	326	3·2	—	3·4	171	5·5	277
0·04	12·4	306	6·1	156	6·0	151	9·6	237
0·06	17·7	293	9·0	152	8·3	140	13·4	221
0·08	23·1	286	12·0	,,	10·6	133	16·8	210
0·10	28·3	282	15·1	,,	13·0	130	20·2	202
0·12	33·6	280	18·3	,,	15·3	128	23·5	196
0·14	38·8	277	21·5	,,	17·6	127	26·7	191
0·16	44·0	275	24·6	,,	20·1	127	30·1	187
0·18	49·3	273	27·2	,,	Changes to brown		33·2	184
0·20	54·5	—	30·2	,,	solution at 40°;		36·2	181
0·24	—	—	36·2	,,	intermediate		42·15	176
0·28	—	—	(42·2)	,,	values to 67°;		48·1	172
0·32	—	—	—		then values for green.		54·05	169

The results show that in aqueous solution, up to $C = 0{\cdot}05$, the rise in C.S.T. due to the violet is nearly double that due to the green. Above this concentration, the ratio becomes progressively less. No reason is known why the former should produce exactly double the effect of the latter, as the value for the complex ion in each case is unknown. The method, however, gives results more in accord with the Werner theory than do either freezing-point or conductivity measurements. The following values were found for chromic nitrate, $Cr(NO_3)_3,9H_2O$ (from Kahlbaum; containing some iron), in *iso*butyric acid:

C.	C.S.T.	e.	E.
0·0138	21·0°	3·1°	225°
0·0505	28·4	10·5	208
0·1207	42·0	24·1	200
0·1692	50·35	32·45	192

Investigation of other salts (*e.g.*, of cadmium) shows that nitrates

do not form complexes and also that the effect of the nitrate radical is much less than that of the chloride. The curve for chromic nitrate lies between the violet and the green, being nearer the latter in the approximate ratio of 5 : 3; hence the ion $[Cr(H_2O)_6]^{\cdots}$ has in aqueous solution nearly the same effect as the $Cr^{\cdots}$ ion, whilst the ion $[CrCl_2(H_2O)_4]^{\cdot}$ has a less effect. These relations are, however, only qualitative (Duckett and Patterson, *J. Physical Chem.*, 1925, **29**, 295). To make them quantitative, the change of hydration with temperature and concentration would have to be taken into account and also the nature of the opposed ion. Under similar conditions of temperature, the values for E are $Cl = 43$, $NO_3 = 11$. At $C = 0{\cdot}05$, E for violet = 300, for green = 154; replacing 3Cl by $3NO_3$ in the violet gives $E = 300 - 129 + 33 = 204$ (Found, for nitrate: 208); replacing Cl by NO_3 in the green gives $154 - 43 + 11 = 122$: hence the effects of $Cr^{\cdots}$ and $CrCl_2(H_2O)_4^{\cdot}$ are in the ratio 175 : 111.

Change in Aqueous Solution.

The method is convenient for investigating rate of change, especially in dilute solutions. As the influence of temperature is very marked, in some cases it is necessary to measure time in minutes, and in others in months.

The results are summarised to supplement those of other workers, who generally used more concentrated solutions, however (*e.g.*, Olie, *Z. anorg. Chem.*, 1906, **51**, 29).

Violet.—Change very slow below 40°, slow below 50°.

$C = 0{\cdot}067$: no change measurable at 40° in 120 mins.

$C = 0{\cdot}073$: 10% at 17° in 3 days; 100% at 95° in 65 mins.

$C = 0{\cdot}188$: 59% at 82° in 22 mins.; 69% at 82° in 57 mins.

(At the ordinary temperature the last had reverted to 16·6% after 4 months, with intermediate values.)

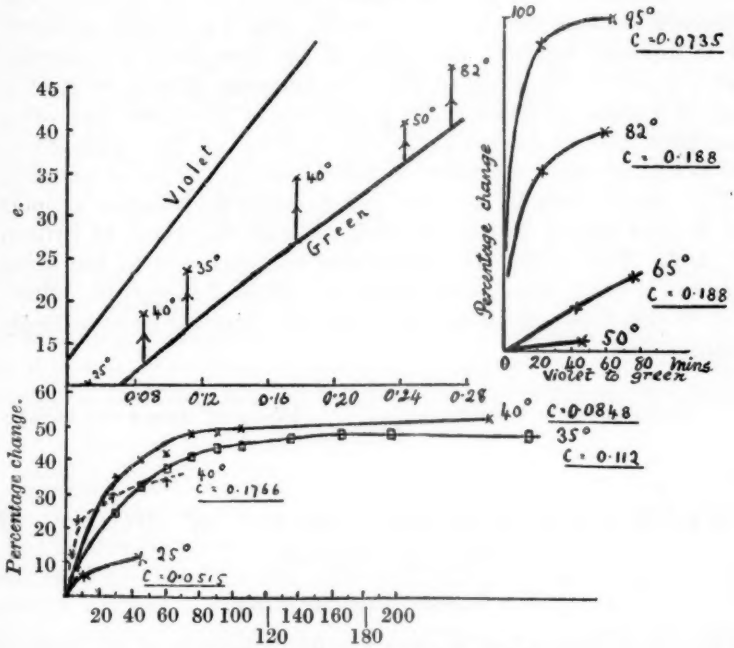
$C = 0{\cdot}188$: 16·6% at 65° in 35 mins.; 26·8% at 65° in 76 mins.; 6·1% at 50° in 47 mins.

Green.—The change is quite appreciable, even at the ordinary temperature. The figures at higher temperatures in the table were obtained by extrapolating the curves shown in Fig. 2 to zero concentration. Equilibrium is practically attained in 2 hours at 40°, 3 hours at 35°, or 24—72 hours at 25°. The position of this equilibrium lies about half-way between the green and the violet up to $C = 0{\cdot}17$ and is almost independent of temperature within this range. At higher concentrations and temperatures, it lies much nearer the green curve. At the ordinary temperature it reverts, during several months, towards the violet. The main results are shown graphically in Fig. 2.

The figures obtained for the system water–phenol, on dissolving the green salt, give $E = 271—204°$, over the temperature range 68—79° and $C = 0{\cdot}00845—0{\cdot}065$. Evidently these values correspond to a mixture; also some reaction with the phenol must be allowed for.

A measurement with the violet in *iso*butyric acid gave $E = 227°$ for $C = 0{\cdot}2587$. Change in hydrolysis must also be considered:

FIG. 2.



although this will not greatly alter the M.M.T., it has been shown to influence the velocity of change.

Solutions in Ethyl Alcohol.

The broken lines in Fig. 1 represent ethyl-alcoholic solutions. The order of salts in ethyl-alcoholic solution has been shown to be nearly the reverse of that in aqueous solution, *e.g.*, salts of tervalent metals have a smaller effect than salts of univalent metals.

The curve C (Fig. 1) for violet up to $e = 20°$ (or a temperature of 40°) lies below that of the green. The dotted line represents a mixture (brown solution) up to $e = 48°$ (or 68°), at which point the curve becomes identical with that of the green, D. It was not

possible to study the kinetics of change in this system. The curve for ferric chloride is given for comparison, as it has been shown that this salt consists of the non-associated molecule $FeCl_3$ in ethyl alcohol, and it is believed that the curve for normal chromic chloride should be very near it.

The molecular influence of water on this system is shown by the bottom line, which has no curvature. It is to be expected that the two molecules of water of hydration in the green isomeride would enter the alcohol and give the corresponding rise of M.M.T. The difference between the two curves varies from 4 to 2 mols. of water. As in aqueous solution, the effect of the complexes is uncertain and it is not to be expected that the difference should be exactly that of 2 mols. of water. The possibility of alcoholate formation also must not be overlooked. The position of the violet curve shows how strongly the water is held in the co-ordinated complex.

The results both in aqueous and in alcoholic solution support the Werner theory and are at variance with the views of Britton (J., 1925, **127**, 2128), who postulates the existence in the green solution of basic aggregates essentially colloidal in nature. Moreover, the effect of colloids on C.S.T. has been shown to be exceedingly small.

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CCCLXX.—*The Dielectric Constants of Mixtures of Organic Liquids.*

By ROBERT NAPIER KERR.

PREVIOUS investigations of the dielectric constants of mixtures of two organic liquids carried out with the object of finding a suitable mixture formula (Silberstein, *Wied. Ann.*, 1895, **56**, 661; Linebarger, *Z. physikal. Chem.*, 1896, **20**, 131; Philip, *ibid.*, 1897, **24**, 18; Dobroserdov, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 679; Grützmacher, *Z. Physik*, 1924, **28**, 342) have paid little attention to other changes which are known to occur on mixing. The simplest of the suggested formulæ is the volumetric rule of Silberstein (*loc. cit.*), *viz.*, $\varepsilon = (\varepsilon_1 v_1 + \varepsilon_2 v_2)/(v_1 + v_2)$, where ε, ε_1, ε_2 are the *D.C.*'s of the mixture and of the two components, respectively, and v_1 and v_2 are the volumes of the two components. This rule results from the definition of the *D.C.* as a property referring to equal volumes of different substances; accordingly, when two liquids are mixed, if it is assumed (1) that the dielectric properties of the two kinds

of molecules remain the same as before mixing, and (2) that the respective molecules retain the same volume in the mixture as in the pure state, it follows that the *D.C.* of the mixture should be given by Silberstein's equation. Dobroserdov investigated a large number of organic mixtures; for several of these approximate agreement was obtained with this rule, but others showed marked deviations. The explanation of these divergences was that chemical compounds were formed between the components of the mixtures, but as in most cases one component was an inert liquid such as benzene, heptane, or carbon tetrachloride, this explanation is scarcely acceptable. Changes in the number of molecules may be caused, however, not only through combination taking place between the two components, but also through changes in the degree of association of one or both. In addition, it is also necessary to consider changes of a more physical nature such as have been discussed by Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1458), *i.e.*, those due to the different environment of the molecules in the mixture from that in the pure state. It appears possible that such changes may be the cause of the deviations noted and, with the object of testing further the validity of the volumetric rule and of ascertaining to what extent deviations from it can be explained in this way, a number of mixtures consisting of benzene as one component and a benzene derivative as the other were investigated.

Experimental.

Method of Determination of Dielectric Constant.—By the use of the thermionic valve an apparatus was constructed for which great accuracy is not claimed, but by means of which the *D.C.* can be determined rapidly and with sufficient accuracy for the present purpose. The actual experimental arrangement is based on a method described by Jackson (*Phil. Mag.*, 1922, **43**, 482) and is similar to that used by Grützmacher (*loc. cit.*). The method gave consistent results as exemplified by those for benzene at $15° \pm 1°$: $\varepsilon = 2{\cdot}28, 2{\cdot}28, 2{\cdot}27, 2{\cdot}29, 2{\cdot}26, 2{\cdot}28, 2{\cdot}27, 2{\cdot}27$: mean, 2·28. After correction for difference of temperature, this value compares favourably with those obtained at 25° by Graffunder (2·268; *Ann. Physik*, 1923, **70**, 225), Grützmacher (2·278; *loc. cit.*), and Isnardi (2·268; *ibid.*, 1922, **9**, 153), but it is rather higher than those given by Sayce and Briscoe (J., 1925, **127**, 315) and by Harris (*ibid.*, p. 1065).

The wave-length used throughout this investigation was 95 metres, *i.e.*, a frequency of approximately 3×10^6 cycles per second.

The results are in Table I: under "Comp." is the composition of the mixture in terms of the percentage by volume of the com-

ponent other than benzene; ε (obs.) are the values of the *D.C.* determined; and "Diff." denotes the deviations from the values calculated from the volume rule. The mixtures were made up by measuring the required volumes by pipettes and checking by weight. The variation of temperature was not more than 0·5° throughout each series. The liquids used were dried over suitable reagents and fractionally distilled until a constant-boiling fraction (within a range of 0·2°) was obtained.

TABLE I.

	Methyl benzoate (12°).		Ethyl benzoate (15°).		Phenetole (15°).		Ethyl cinnamate (16°).	
Comp.	ε (obs.).	Diff.	ε (obs.).	Diff.	ε (obs.).	Diff.	ε (obs.).	Diff.
0	2·28	—	2·28	—	2·28	—	2·28	—
20	3·18	+0·01	3·09	+0·04	2·63	−0·05	3·03	+0·05
40	4·04	−0·02	3·85	+0·03	3·12	+0·01	3·74	+0·05
60	4·93	−0·01	4·59	+0·01	3·53	−0·01	4·42	+0·02
80	5·82	−0·01	5·32	−0·03	3·95	±0·00	5·14	+0·02
100	6·72	—	6·12	—	4·37	—	5·83	—
	Dimethylaniline (14°).		Chlorobenzene (15°).		Bromobenzene (16°).		Aniline (14°).	
0	2·28	—	2·27	—	2·28	—	2·28	—
5	2·51	+0·09	2·47	+0·03	—	—	—	—
10	2·65	+0·09	2·62	+0·01	2·65	+0·05	—	—
15	2·83	+0·14	2·88	+0·10	—	—	—	—
20	3·02	+0·19	3·04	+0·09	2·99	+0·07	3·16	−0·11
40	3·52	+0·13	—	—	3·60	+0·05	4·05	−0·21
50	—	—	4·04	+0·07	—	—	—	—
60	4·07	+0·13	—	—	4·21	+0·02	5·02	−0·24
80	4·63	+0·13	4·99	±0·00	4·81	−0·01	6·07	−0·19
100	5·05	—	5·67	—	5·46	—	7·20	—
	Benzaldehyde (15°).		Nitrobenzene (15°).		Benzyl alcohol (14°).		*m*-Cresol (16°).	
0	2·28	—	2·28	—	2·28	—	2·28	—
20	4·81	−0·63	6·74	−2·49	3·37	−1·18	3·28	−1·13
40	7·46	−1·13	11·90	−3·48	4·86	−1·86	4·82	−1·73
60	10·57	−1·28	18·19	−3·74	7·46	−1·63	6·95	−1·73
80	13·92	−0·99	25·81	−2·67	10·58	−0·78	9·86	−0·96
100	18·07	—	35·03	—	13·63	—	12·95	—

Discussion of Benzene Mixtures.

A number of these mixtures obey the volumetric rule fairly accurately. On the other hand, marked deviations are obtained for the mixtures of benzene with aniline, benzaldehyde, *m*-cresol, benzyl alcohol, or nitrobenzene, which have curves (*D.C.*–volumetric composition) convex to the axis of concentration to a varying extent. These substances, however, all show association in benzene solution (Turner, "Molecular Association," Appendix), and thus a simple explanation is available for the divergences of these mixtures. According to Debye's theory of dielectrics (*Physikal. Z.*, 1912, **13**, 97), molecules possess permanent dipoles. When two

molecules associate, the new complex has a different moment and, if it be assumed that the association takes place so that the net effect is a partial neutralisation of the moments of the individual dipoles, this moment will be smaller than the sum of the original moments, thus causing a fall in the dielectric properties of the substance. As those substances which have normal molecular weights in benzene give linear curves for the *D.C.* when mixed with that solvent, we can safely attribute the marked divergences of the mixtures of benzene with aniline, benzaldehyde, nitrobenzene, benzyl alcohol, or *m*-cresol to the association known to occur in the mixtures.

With several mixtures, there is a deviation from the straight line which, although slight, is of the same nature for each mixture. The best example is benzene–dimethylaniline, but similar deviations obtain for chloro- and bromo-benzene with benzene and to a less marked degree for benzene–ethyl cinnamate. The values of the *D.C.*'s for these mixtures are all slightly greater than those required by the volume rule and the deviations are greatest at low concentrations of the benzene derivative: the corresponding curves are approximately linear down to concentrations of about 20%, but after that point they show a distinct drop. Although these deviations are very slight, the fact that they occur in the same manner for several mixtures seems to testify to their actual existence and requires an explanation.

Only changes in the degree of association have up till now been considered. As mentioned above, however, the physical effect of the difference of the cohesive forces acting on the molecules in the mixture also requires attention; in previous discussions of the *D.C.*'s of mixtures differences of this nature have been ignored. When a liquid is subjected to an alternating electric field, as when the *D.C.* is determined, the molecules may be considered to be maintained in a state of rapid vibration (Debye, *Verh. deut. physikal. Ges.*, 1913, **15**, 777); the amount of this vibration depends partly on the strength of the external field, the size of the dipoles, and the heat motions of the molecules, but also on the cohesive forces between neighbouring molecules. These forces will not in general be the same in a mixture as in the component substances, and the amplitude with which a molecule vibrates for a given external field will undergo a slight change on mixing: this will have an effect on the dielectric action of the molecules. Thus, if the cohesive forces acting in a liquid A are smaller than those in a liquid B, then, when A and B are mixed, the forces acting on B molecules will be smaller in the mixture than in B itself and, accordingly, the molecules will have a greater freedom of vibration, thus causing the contribution

which they make to the dielectric action of the mixture to be larger than predicted by the mixture rule. Such effects should be greatest at low concentrations, and the greatest divergences for the *D.C.*'s of the mixtures under consideration occur also at low concentration.

The internal pressure as calculated by Hildebrand (*loc. cit.*) is the only available measure of these cohesive forces in the liquid state, and with the object of testing the above hypothesis the relative internal pressures (π) for these substances have been calculated from surface tension data (Landolt-Börnstein's Tabellen). The formula used was $\pi = \gamma/v^{1/3}$, where γ and v are the surface tension and molecular volume, respectively, and the values are in Table II.

TABLE II.

Relative Internal Pressures at 20°.

Benzene	6·54	Chlorobenzene	7·05
Ethyl benzoate	6·61	Bromobenzene	7·50
Methyl benzoate	(7·44)	Dimethylaniline	7·28
Phenetole	6·46	Ethyl cinnamate	6·73

According to this explanation, the internal pressures of those substances the mixtures of which with benzene have abnormally high values of the *D.C.* should be greater than that of benzene, whereas those substances which obey the volumetric rule accurately in benzene solution should have internal pressures approximately equal to that of benzene. Table II shows that this is actually the case with the single exception of methyl benzoate: chlorobenzene, bromobenzene, and dimethylaniline all have values decidedly higher than benzene, and ethyl cinnamate, the mixture of which with benzene shows only a slight deviation, occupies an intermediate position with a value only slightly greater than that for benzene; ethyl benzoate and phenetole, on the other hand, have values approximately equal to that for benzene. The internal pressure calculated for methyl benzoate seems anomalous when compared with that of ethyl benzoate, for the two esters resemble each other closely in other properties, both in the pure state and in mixtures; it appears quite possible, therefore, that the value calculated for methyl benzoate is based on incorrect data. With this single doubtful exception, then, these figures indicate that those mixtures, of which the two components have nearly equal internal pressures and therefore approach closely to ideal solutions, obey the simple volumetric mixture rule, and, further, that internal pressure differences between the two components of a non-associating mixture cause slight deviations from this rule.

The foregoing considerations show that both chemical and physical changes on mixing must be taken into account in discussing

the dielectric constants of mixtures. For polar substances, Hildebrand (*loc. cit.*, p. 1461) states that the former effects outweigh the latter, and this is evident from those mixtures in which association occurred. It is possible, however, that at low dilutions, where the physical effects are greatest, such changes may cause quite an appreciable effect even with polar substances. Partington and Rule (*Phil. Mag.*, 1926, **1**, 1035) have investigated a number of dilute solutions of organic solids and observe that for benzene–benzoic acid the *D.C.* increases with concentration to a maximum at about 1% concentration and then decreases; no explanation was brought forward for this behaviour, and it is now suggested that this is an example of physical changes causing an appreciable effect at low concentrations but becoming negligible in comparison with association changes at higher concentrations.

Mixtures containing Ether as One Component.

In the benzene mixtures no case has been obtained where the *D.C.* of the mixture is much higher than that required by the volume rule. Dobroserdov (*loc. cit.*), however, describes a number of mixtures which have curves concave to the axis of concentration and show marked deviations, *e.g.*, with ether–chloroform (compare Philip, *Z. physikal. Chem.*, 1897, **24**, 18) the *D.C.* attains a maximum value higher than that of either component. These mixtures all contain an ether as one component and, in order to enquire further into their nature, a number of mixtures of ethyl ether with benzene derivatives have been examined: the results are in Table III, "Comp." denoting the volume percentage of the component other than ether.

TABLE III.

	Dimethylaniline (17°).		Benzaldehyde (18°).		*m*-Cresol (17°).	
Comp.	ϵ (obs.).	Diff.	ϵ (obs.).	Diff.	ϵ (obs.).	Diff.
0	4·40	—	4·35	—	4·41	—
20	4·56	+0·03	6·97	−0·03	5·94	−0·24
40	4·65	−0·01	9·65	±0·00	7·49	−0·30
60	4·80	+0·02	12·38	+0·09	9·15	−0·33
80	4·90	−0·01	15·01	+0·07	11·00	−0·16
100	5·04	—	17·59	—	12·85	—
	Nitrobenzene (20°).		Chlorobenzene (15°).		Aniline (15°).	
0	4·35	—	4·46	—	4·44	—
20	9·51	−0·75	4·79	+0·08	5·58	+0·62
40	15·07	−1·10	5·06	+0·10	6·30	+0·82
60	20·88	−2·21	5·37	+0·17	6·70	+0·70
80	27·26	−0·74	5·58	+0·13	6·98	+0·46
100	33·91	—	5·70	—	7·04	—

In the above series there are again instances of mixtures which obey the volumetric mixture rule fairly accurately; from what

has been proved for the benzene series these mixtures—ether with benzaldehyde and with dimethylaniline—can be accepted as normal and the deviations of the others from this rule must be attributed to changes on mixing. Two mixtures—ether with *m*-cresol and with nitrobenzene—have curves deviating only slightly from the straight line with values smaller than those required. This is in good accord with the association changes discussed for the benzene series, and with the fact that polar substances which have abnormal molecular weights in inert solvents give practically normal values in ether (Turner, *op. cit.*); the slight deviations show that association still takes place, but to a much smaller extent, causing the observed lowering of *D.C.* The remaining mixtures—with aniline or chlorobenzene—have curves concave to the axis of concentration and resemble those described by Dobroserdov. The difference between these two mixtures and the other four cannot be attributed to differences of internal pressure, since all the liquids mixed with ether in this series are alike in having much higher internal pressures than ether. It appears, therefore, that some chemical explanation must be sought.

In the discussion of benzene mixtures, the only type of association product considered was that which caused a partial neutralisation of the moments of the participating molecules, *i.e.*, the dipoles joined laterally; Ebert (*Z. physikal. Chem.*, 1924, **113**, 1), however, suggests that another type is possible in which the dipoles join end-on. This association gives a product with a moment equal to the sum of the moments of the participating dipoles, but, as the polarisation produced is proportional to the square of the moment of the dipole (Lange, *Z. Physik*, 1925, **33**, 169), the net effect is to cause an increase of the dielectric properties and not a decrease as with the association previously considered. The nature of the association product formed is determined by the sizes of the dipoles and their geometrical positions in the participating molecules. If association takes place between molecules of the same kind, the two dipoles, being of the same size, will be able to fit easily together, giving association of the first type and causing a fall of *D.C.* as found with substances associating in benzene solution. Association, however, may also take place between molecules of different substances and, when this occurs, there may be considerable differences in the sizes of the molecules and in the geometrical positions of the dipoles in the molecules. In consequence, the dipoles are not able to fit together in the above manner, but, instead, they may join end-on, giving association of the second type which produces a rise in dielectric properties. The most suitable conditions for this kind of association obtain with the mixtures under discussion, for

ether has a small molecule compared with the benzene derivatives, and the sizes of the dipoles in the two molecules will be quite different. A simple explanation of the abnormally high values of the *D.C.* obtained in some cases is thus afforded by association of this kind.

It appeared of interest to obtain further evidence that these different kinds of association can take place from mixtures of liquids which would be expected, from chemical evidence, to show some tendency to combine. Mixtures of aniline–*m*-cresol and of acetone–chloroform (which under certain conditions form a compound) were therefore investigated; the results are in Table IV, from which it is seen that these two mixtures behave in quite

TABLE IV.

Acetone–Chloroform (17°).			*m*-Cresol–Aniline (17°).		
Comp.	ϵ (obs.).	Diff.	Comp.	ϵ (obs.).	Diff.
0	4·85	—	0	7·04	—
20	9·37	+1·31	20	7·87	−0·36
40	12·84	+1·57	40	8·62	−0·80
60	15·67	+1·20	50	9·03	−0·98
80	18·32	+0·64	60	9·47	−1·13
100	20·89	—	80	10·45	−1·34
			100	12·98	—

different manners, the acetone–chloroform mixture having higher and *m*-cresol–aniline lower values than required by the mixture rule. This suggests that the two different kinds of association to which reference has been made are occurring in these mixtures, the second type taking place in the former and the first type in the latter case. This is in good agreement with the conditions already mentioned for formation of the two kinds. In *m*-cresol and aniline, the molecules are of nearly the same size and accordingly fit together easily, giving association of the first type; on the other hand, acetone and chloroform have molecules bearing no relationship to each other in structure and thus, since the dipoles are of different sizes, association of the second type takes place. These results, therefore, support the view that different kinds of products can be formed when association takes place and that the nature of the product formed depends on the relative sizes and shapes of the dipoles in the participating molecules.

Summary.

The dielectric constants of a number of mixtures of benzene derivatives with benzene have been determined. Those mixtures which approach most closely to ideal solutions obey the simple volumetric-mixture rule. Differences in internal pressure between the components of non-associating mixtures cause slight deviations

from this rule. Association taking place in these mixtures causes a lowering of dielectric properties. A number of mixtures of benzene derivatives with ether have also been examined, and with some of these the dielectric constants are considerably greater than those required by the volumetric rule. From these results it is concluded that the effect of association on the dielectric constant depends on the nature of the complex formed, and this is determined by the sizes and shapes of the participating dipoles. This view is supported by results obtained with acetone–chloroform and *m*-cresol–aniline mixtures.

The author wishes to express his thanks to Professor Sir James Walker, F.R.S., for his interest and helpful suggestions during the research, to the Carnegie Trust for the Universities of Scotland for a research scholarship during the tenure of which part of this work was carried out, and to Messrs. Brunner Mond and Co. for a grant defraying the cost of the apparatus used.

EDINBURGH UNIVERSITY. [*Received, July 28th*, 1926.]

CCCLXXI.—*Derivatives of Stilbene.*

By JULIUS NICHOLSON ASHLEY.

THIELE and ESCALES (*Ber.*, 1901, **34**, 2842) have shown that 2 : 4-dinitrostilbene is reduced to 2-nitro-4-aminostilbene by ammonium sulphide in boiling alcoholic solution and to the isomeric nitroamine by stannous chloride. This suggested that the very readily accessible condensation products of aromatic aldehydes and 2 : 4-dinitrotoluene might be transformed into phenanthrene derivatives by following one of two routes, but unfortunately neither of these has proved to be practicable. All attempts to obtain a phenanthrene derivative from 4-nitro-2-aminostilbene and from 4-nitro-2-amino-3′ : 4′-methylenedioxystilbene,

$$NO_2\cdot C_6H_3(NH_2)\cdot CH{:}CH\cdot C_6H_3{:}O_2CH_2$$

(Gulland, Robinson, and Stafford, J., 1925, **127**, 1502), by treatment of the diazo-derivatives with copper powder were fruitless. In order to test the less direct process, in a case which was considered to be a favourable one, *2-nitro-4-amino-3′ : 4′-dimethoxystilbene*,

$$NO_2\cdot C_6H_3(NH_2)\cdot CH{:}CH\cdot C_6H_3(OMe)_2 \text{ (I)},$$

was converted into *4-chloro-2-nitro-3′ : 4′-dimethoxystilbene*,

$$NO_2\cdot C_6H_3Cl\cdot CH{:}CH\cdot C_6H_3(OMe)_2 \text{ (II)},$$

and then into *4-chloro-2-amino-3′ : 4′-dimethoxystilbene*,

$$NH_2\cdot C_6H_3Cl\cdot CH{:}CH\cdot C_6H_3(OMe)_2 \text{ (III)}.$$

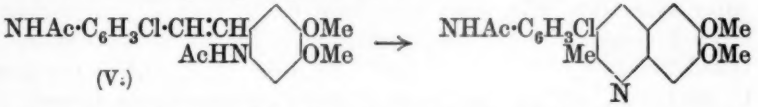
When an aqueous or alcoholic suspension of the corresponding

diazonium sulphate was treated with copper powder, the only isolable product was an amorphous nitrogenous compound.

The chloronitrodimethoxystilbene (II) is readily nitrated, yielding, doubtless, 4-*chloro*-2 : 6′-*dinitro*-3′ : 4′-*dimethoxystilbene*,

$$NO_2 \cdot C_6H_3Cl \cdot CH{:}CH \cdot C_6H_2(OMe)_2 \cdot NO_2 \quad (IV),$$

and after reduction and acetylation this affords 4-*chloro*-2 : 6′-*diacetylamino*-3′ : 4′-*dimethoxystilbene* (V). Gulland, Robinson, and Stafford (*loc. cit.*) mention the possibility that *oo*′-diacylaminostilbenes might be dehydrated (losing $2H_2O$) with formation of 2 : 6-naphthyridines, but the substance (V) loses only $1H_2O$ when it is heated with phosphoryl chloride.



(V.)

Only one of the possible directions of condensation is represented in the above scheme.

Experimental.

2-*Nitro*-4-*amino*-3′ : 4′-*dimethoxystilbene* (I).—Hydrogen sulphide was passed for 3 hours through a gently refluxing mixture of 2 : 4-dinitro-3′ : 4′-dimethoxystilbene (20 g.; Gulland, Robinson, and Stafford, *loc. cit.*), alcohol (250 c.c.), and aqueous ammonia (40 c.c.; *d* 0·880). After cooling, the bright red, crystalline solid was collected and heated for 2 hours with an excess of carbon disulphide, in which it was very sparingly soluble. The residual amine (78% yield) crystallised from *iso*butyl alcohol in bright red prisms, m. p. 186—187° (Found: C, 63·7; H, 5·5. $C_{16}H_{16}O_4N_2$ requires C, 64·0; H, 5·4%). 2-Nitro-4-amino-3′ : 4′-dimethoxystilbene is readily soluble in acetone, ethyl acetate, or chloroform, moderately readily soluble in alcohol or acetic acid, and very sparingly soluble in carbon tetrachloride or carbon disulphide. The solutions in the last two cases exhibited a weak green fluorescence. The *hydrochloride*, prepared by the action of alcoholic hydrogen chloride, formed long, golden needles melting at 223° with previous darkening at 200° (Found: Cl, 10·5. $C_{16}H_{16}O_4N_2$,HCl requires Cl, 10·5%). The *acetyl* derivative crystallised from dilute acetic acid in pale orange parallelipipeds, m. p. 183—184° (Found: C, 62·9; H, 5·3. $C_{18}H_{18}O_5N_2$ requires C, 63·2; H, 5·3%). Oxidation of this acetyl derivative with potassium permanganate in the presence of magnesium sulphate yielded a mixture of veratric and 2-nitro-4-acetylaminobenzoic acids. The latter acid melted at 219°, alone or mixed with an authentic specimen. This proves that it is the *p*-nitro-group in the original stilbene which is reduced by ammonium sulphide.

4-Chloro-2-nitro-3′ : 4′-dimethoxystilbene (II).—A hot solution of 2-nitro-4-amino-3′ : 4′-dimethoxystilbene (20 g.) in glacial acetic acid (225 c.c.) was poured into a cold solution of cupric sulphate (40 g.) in hydrochloric acid (1000 c.c. of 15%), and the mixture cooled to 0°. Sodium nitrite (24 g.) in water (100 c.c.) was gradually added with stirring. The chocolate-coloured mixture was then poured slowly into an almost boiling solution of cuprous chloride (prepared from cupric sulphate, 45 g., sodium chloride, 22 g., water, 110 c.c., concentrated hydrochloric acid, 300 c.c., and an excess of copper) and vigorously shaken. Copper bronze (20 g.) was then introduced, and next day the solid was collected, washed, and thoroughly dried. After extraction with light petroleum (b. p. 60—80°), a product separating in orange, leaf-like crystals, m. p. 124—125°, was obtained (yield 22—24%) (Found : C, 60·1; H, 4·6. $C_{16}H_{14}O_4NCl$ requires C, 60·1; H, 4·4%). 4-Chloro-2-nitro-3′ : 4′-dimethoxystilbene is readily soluble in most organic solvents, and dissolves in sulphuric acid to a dull green solution.

4-Chloro-2-amino-3′ : 4′-dimethoxystilbene (III).—A solution of 4-chloro-2-nitro-3′ : 4′-dimethoxystilbene (5 g.) in glacial acetic acid (70 c.c.) was treated alternately with small quantities of hydrochloric acid (30 c.c. in all) and zinc dust (10 g.). The amine, which was precipitated on the addition of excess of dilute aqueous ammonia, crystallised from alcohol in very pale brown prisms, m. p. 147—148° [Found : C, 66·0; H, 5·6; MeO, 21·35. $C_{14}H_{10}NCl(OMe)_2$ requires C, 66·3; H, 5·5; MeO, 21·4%]. The pale brown solution of the amine in ether, benzene, or ethyl acetate exhibits an intense violet fluorescence; a solution in acetone fluoresces with a slightly more bluish tinge. The *hydrochloride* and *sulphate* are stable in the presence of the corresponding acid, but are hydrolysed by water. The *acetyl* derivative crystallised from alcohol in white needles, m. p. 180° [Found : MeO, 18·6. $C_{16}H_{12}ONCl(OMe)_2$ requires MeO, 18·7%]. A trace of the acetyl compound dissolved with a very pale brown colour in concentrated sulphuric acid. Addition of a crystal of potassium nitrate produced a purple coloration, which quickly changed to yellowish-brown.

4-Chloro-2 : 6′-dinitro-3′ : 4′-dimethoxystilbene (IV).—4-Chloro-2-nitro-3′ : 4′-dimethoxystilbene (3 g.) was triturated with glacial acetic acid (6 c.c.), and nitric acid (5 c.c.; *d* 1·42) gradually added. The yellow solid obtained on the addition of water crystallised from glacial acetic acid in yellow needles, m. p. 175° (Found : C, 52·5; H, 3·8. $C_{16}H_{13}O_6N_2Cl$ requires C, 52·7; H, 3·6%). This dinitro-derivative is readily soluble in chloroform, benzene, ethyl acetate, or acetone, and moderately readily soluble in alcohol.

4-Chloro-2 : 6′-diacetylamino-3′ : 4′-dimethoxystilbene (V).—Zinc

dust (12 g.) and hydrochloric acid (30 c.c. in all) were added alternately to a solution of 4-chloro-2 : 6′-dinitro-3′ : 4′-dimethoxystilbene (3 g.) in glacial acetic acid (60 c.c.). After filtration, an excess of aqueous ammonia was added, and the crude diamine (which dissolved readily in ether, forming a brown solution with an intense sky-blue fluorescence) was acetylated by acetic anhydride (10 c.c.) in the cold. The product (yield, 60%) crystallised from glacial acetic acid in pale yellow rods, m. p. 275° (decomp.) (Found : C, 61·4; H, 5·4. $C_{20}H_{21}O_4N_2Cl$ requires C, 61·8; 5·4%). This diacetyl compound is soluble in alcohol or acetone, and very sparingly soluble in most other solvents. A minute amount of the substance dissolved in concentrated sulphuric acid to a pale pink solution, which was momentarily decolorised and then became yellow on the addition of a crystal of potassium nitrate.

Action of phosphoryl chloride on 4-chloro-2 : 6′-diacetylamino-3′ : 4′-dimethoxystilbene. The deep blood-red solution obtained by heating the diacetylamino-compound (2 g.) with phosphoryl chloride (10 c.c.) on the steam-bath for 4 hours was poured slowly into cold caustic soda (250 c.c. of 12%). The pale brown precipitate was triturated with carbon disulphide, and the residue was extracted with chloroform. On the addition of twice the volume of light petroleum (b. p. 60—80°), a deep brown material was precipitated, and the filtrate, after the addition of a little more light petroleum, deposited a pale brown solid melting at about 230° (decomp.) after darkening at 160° (Found : C, 64·4; H, 5·3; N, 7·9. $C_{20}H_{19}O_3N_2Cl$ requires C, 64·8; H, 5·1; N, 7·55%). The substance, which could not be crystallised, contained no diazotisable amino-group, but after it had been heated for a short time with hydrochloric acid, diazotisation, followed by coupling with β-naphthol in alkaline solution, gave a red azo-compound.

I wish to thank Professor R. Robinson, F.R.S., for his interest in this research, and the Chemical Society for a grant which has defrayed a part of the expense involved.

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CCCLXXII.—*A Synthesis of Some Substituted 3-Methylquinolines.*

By STANLEY GORDON WILLIMOTT and IAN ALEXANDER SIMPSON.

THE earlier methods for the synthesis of 3-methylquinoline (Riedel, *Ber.*, 1883, **16**, 1610; Doebner and Miller, *Ber.*, 1884, **17**, 1714; 1885, **18**, 1642; Miller and Kinkelin, *Ber.*, 1887, **20**, 1916) give

poor yields and are useless when substituted derivatives are required. Koenigs and Bischkopf (*Ber.*, 1901, **34**, 4330) claim to have synthesised 3-methylquinoline in good yield by condensing *o*-aminobenzaldehyde and propaldehyde in the presence of 1% potassium hydroxide. Under these conditions, however, Wislicenus and Elvert (*Ber.*, 1909, **42**, 1145) obtained only an oily intermediate product that gave no picrate; but they prepared the pure base in an 80% yield by heating together equimolecular quantities of *o*-aminobenzaldehyde and propaldehyde in a bomb tube at 220°. As 3-methylquinoline was required in quantity, the bomb-tube method of Wislicenus and Elvert was discarded, and a further modification of the Friedländer type of synthesis was attempted by condensing together equimolecular proportions of *o*-aminobenzaldehyde and propaldehyde in aqueous alcohol, piperidine being used as a condensing agent. The compound isolated was, however, a syrup which gave none of the characteristic reactions of a quinoline and resembled the intermediate oily compound obtained by Wislicenus and Elvert under similar conditions. The substance probably has the structure

$$NH_2 \cdot C_6H_4 \cdot CH(OH) \cdot CHMe \cdot CH{:}N \cdot C_6H_4 \cdot CHO$$

analogous to that ascribed by Sonn and Benirschke (*Ber.*, 1921, **54**, 1731) to the compound obtained by condensing 6-aminopiperonal and acetaldehyde by means of dilute alkali.

Heller (*Ber.*, 1910, **43**, 1917) describes a synthesis of 3-methylquinoline from *o*-nitrobenzaldehyde and propaldehyde in which an excess of bisulphite solution is used as condensing agent and the intermediate aldol compound is reduced to the quinoline base by means of zinc dust and acetic acid. A modification of this method using piperidine instead of bisulphite as the condensing agent was found to be most suitable for the preparation of 3-methylquinoline and its substituted derivatives. In two cases, however, it was found preferable to form the styryl derivative by treatment of the aldol with acetic anhydride (compare Borsche and Quast, *Ber.*, 1919, **52**, 432) and reduce this with stannous chloride and hydrochloric acid. The substituted bases, which were only obtained in relatively poor yield, could usually be isolated as crystalline solids. They decompose rapidly to red oils on exposure to air, form characteristic quaternary salts, and, with the exception of 6:7-dimethoxy-3-methylquinoline, are volatile in steam. The dilute aqueous solutions of the hydrochlorides of these bases exhibit a characteristic bluish-green fluorescence.

Experimental.

β-*o*-*Nitrophenyl*-α-*methylhydracrylaldehyde*.—The deep red solution obtained by keeping an alcoholic solution of *o*-nitrobenzaldehyde

(1 mol.), propaldehyde (1½ mols.), and a few drops of piperidine for 5 days at room temperature was diluted with water. The aldol, isolated by means of ether and purified in alcoholic solution by charcoal, was obtained (yield, 80%) as a clear yellow syrup which showed no tendency to crystallise and could not be distilled under reduced pressure without decomposition (compare Heller, *loc. cit.*) (Found: C, 57·3; H, 5·9; N, 6·7. Calc. for $C_{10}H_{11}O_4N$: C, 57·4; H, 5·3; N, 6·7%).

3-Methylquinoline was obtained by reducing β-*o*-nitrophenyl-α-methylhydracrylaldehyde with zinc dust and acetic acid in the way described by Heller (yield, 25% calc. on the nitrobenzaldehyde).* The chloroplatinate crystallises in orange-red needles, m. p. 249° (compare Miller and Kinkelin, *Ber.*, 1887, **20**, 1917) [Found: Pt, 26·8; H_2O, 5·0. Calc. for $(C_{10}H_9N)_2,H_2PtCl_6,2H_2O$: Pt, 26·7; H_2O, 4·9%]. The *ethiodide* crystallises from absolute alcohol in yellow plates, m. p. 220° (decomp.) (Found: I, 43·2. $C_{12}H_{14}NI$ requires I, 42·4%). The *silver nitrate* double salt crystallises from alcohol in lustrous, silvery plates, m. p. 180°. The *dichromate* crystallises from hot water in red prisms, m. p. 134°.

6 : 7-*Methylenedioxy*-3-*methylquinoline*.—A solution of 6-nitropiperonal (35 g.), propaldehyde (20 g.), and piperidine (2 c.c.) in 70% alcohol (2 l.) having been kept for 5 days at room temperature, the alcohol was distilled off and the resultant heavy red oil, presumably β-6-nitro-3 : 4-methylenedioxyphenyl-α-methylhydracrylaldehyde, reduced as previously described. The mixture was made alkaline and the base distilled in steam. The green, milky distillate slowly deposited 6 : 7-*methylenedioxy*-3-*methylquinoline* in long, colourless needles (+ $2H_2O$), m. p. 74°, which, when dried over sulphuric acid, crumbled to a fine, white powder, the anhydrous base melting at 105—106° (yield, 18% calc. on 6-nitropiperonal) (Found for the hydrated base: H_2O, 16·0. $C_{11}H_9O_2N,2H_2O$ requires H_2O, 16·1%. Found for the anhydrous base: C, 70·4; H, 4·8; N, 7·5. $C_{11}H_9O_2N$ requires C, 70·6; H, 4·8; N, 7·5%). The *chloroplatinate* crystallises from water in orange-yellow plates [Found: Pt, 24·7. $(C_{11}H_9O_2N)_2,H_2PtCl_6$ requires Pt, 24·9%]. The *chloroaurate* separates from dilute hydrochloric acid in golden-yellow needles (Found: Au, 37·3. $C_{11}H_9O_2N,HAuCl_4$ requires Au, 37·4%). The *picrate* forms yellow needles, m. p. 259°. The *methiodide*, prepared by refluxing equimolecular proportions of the base and methyl iodide in anhydrous benzene, crystallises from

* It has since been found that by reducing this substance with stannous chloride and hydrochloric acid in the way described in the preparation of 6 : 7-dimethoxy-3-methylquinoline the yield of 3-methylquinoline can be increased to 80%.

absolute alcohol in yellow needles, m. p. 240° (Found: I, 38·6. $C_{12}H_{12}O_2NI$ requires I, 38·5%). The *ethiodide* forms yellow needles, m. p. 195°.

β-6-*Nitro*-3 : 4-*dimethoxyphenyl*-α-*methylhydracrylaldehyde* can be obtained in extremely poor yield from 6-nitroveratraldehyde by the method previously described. By using an excess of propaldehyde and no other solvent, however, the aldol is obtained, in 30% yield, as a pale brown syrup with a characteristic odour. Its alcoholic solution exhibits a strong green fluorescence.

6-*Nitro*-3 : 4-*dimethoxy*-α-*methylcinnamaldehyde*. — The preceding aldol (5 g.) was boiled with acetic anhydride (25 g.) under reflux for 3 hours and the cooled, dark brown solution was poured into excess of dilute sodium hydroxide solution, cooled with ice. The brown solid which slowly separated crystallised from benzene in yellow needles, m. p. 165—166° (Found: C, 57·3; H, 5·1. $C_{12}H_{13}O_5N$ requires C, 57·4; H, 5·2%).

6 : 7-*Dimethoxy*-3-*methylquinoline* can be obtained in very poor yield by direct reduction of the aldol compound with zinc dust and acetic acid. A more satisfactory method is as follows: 6-Nitro-3 : 4-dimethoxy-α-methylcinnamaldehyde (2 g.) was added slowly to a boiling solution of stannous chloride (20 g.) in concentrated hydrochloric acid (50 c.c.). The cooled, dark red solution was made alkaline, and the base extracted with ether. The ethereal solution was shaken with dilute hydrochloric acid (traces of tarry matter, which increase greatly if the initial material is not pure, are retained by the ether), and the base, after being liberated, was again dissolved in ether and dried over anhydrous sodium sulphate; the ethereal solution was then saturated at 0° with dry hydrogen chloride. The precipitated *hydrochloride* crystallised from alcohol in small, colourless needles, m. p. 220—223° (decomp.) (Found: Cl, 14·9. $C_{12}H_{13}O_2N,HCl$ requires Cl, 14·8%). The base, which rapidly decomposes to a dark brown oil on exposure to air, crystallises from ether in long, colourless needles, m. p. 81—83°. The *methiodide* forms pale yellow needles, m. p. 245° (decomp.).

6-*Nitro*-3-*methoxy*-α-*methylcinnamaldehyde*. — 6-Nitro-3-methoxybenzaldehyde (Heilbron, Kitchen, Parkes, and Sutton, J., 1925, **127**, 2172), treated with propaldehyde and piperidine by the method for the preparation of β-6-nitro-3 : 4-dimethoxyphenyl-α-methylhydracrylaldehyde, gave a golden-yellow oil, presumably β-3-methoxyphenyl-α-methylhydracrylaldehyde. This was converted, by means of acetic anhydride, into the *cinnamaldehyde*, which crystallised from benzene in pale yellow plates, m. p. 115—116° (Found: C, 60·0; H, 5·1. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%).

6-*Methoxy*-3-*methylquinoline*.—The above aldehyde was reduced

with stannous chloride and concentrated hydrochloric acid and the reaction mixture was made alkaline and distilled in steam. The distillate was extracted with ether, and the *hydrochloride* precipitated from the dried ethereal solution. It crystallised from alcohol in colourless plates, m. p. 213—215° (Found : Cl, 16·7. $C_{11}H_{11}ON,HCl$ requires Cl, 16·9%). Attempts to isolate the base produced a colourless oil which could not be crystallised and rapidly developed a red colour on exposure to air. The *methiodide* crystallises from methyl alcohol in yellow needles, m. p. 280—283° (decomp.) (Found : I, 39·9. $C_{12}H_{11}ONI$ requires I, 40·3%). The *chloroplatinate* forms golden needles [Found : Pt, 25·5. $(C_{11}H_{11}ON)_2,H_2PtCl_6$ requires Pt, 25·8%].

The authors desire to thank Professor I. M. Heilbron, D.S.O., D.Sc., for his interest in this work and his valuable advice. They are also indebted to the Advisory Council of the Department of Scientific and Industrial Research and to the Trustees of the late Professor Campbell Brown for grants which enabled the work to be carried out.

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CCCLXXIII.—*The Chemistry of Cadinene. Part II. Compounds related to Cadinene.*

By GEORGE GERALD HENDERSON and JOHN MONTEATH ROBERTSON.

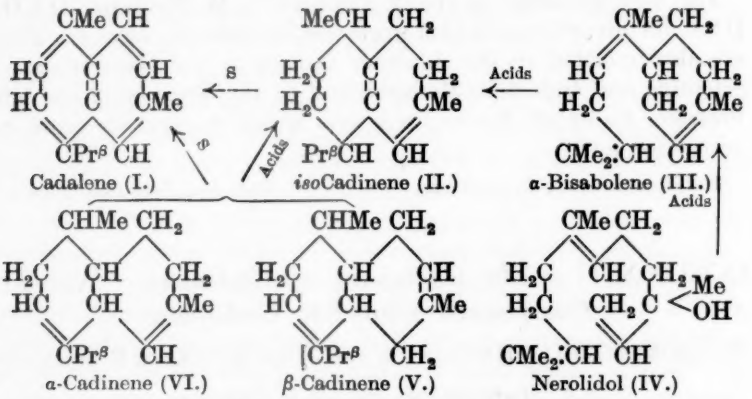
A. *Hydrocarbons related to Cadinene.*

IN the present paper, it is shown that (*a*) the *iso*cadinene described by Henderson and A. Robertson (J., 1924, **125**, 1992) and (*b*) the sesquiterpene isolated from cade oil by Tröger and Feldmann (*Arch. Pharm.*, 1898, **236**, 692) and subsequently investigated by Lepeschkin (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 126) are probably identical and differ from cadinene only in the positions of the double bonds. Both sesquiterpenes must be hexahydrocadalenes, since they yield cadalene on dehydrogenation by Ruzicka's method (*Helv. Chim. Acta*, 1921, **4**, 505).

From a comparison of the physical and chemical properties, it seems reasonable to suggest that *iso*cadinene may be represented by (II), which is the formula provisionally assigned by Ruzicka and Capato (*Helv. Chim. Acta*, 1925, **8**, 259) to the hexahydrocadalene synthesised by them from nerolidol (IV) and bisabolene (III) by the action of acid reagents. A comparison of the physical properties of *iso*cadinene, the cade oil sesquiterpene, and Ruzicka and Capato's synthetic hexahydrocadalene is given below :

	B. p./11—12 mm.	d.	n_D.
*iso*Cadinene	124—126°	0·914	1·515
Cade oil sesquiterpene	124—128	0·918	1·515
Synthetic hexahydrocadalene	125—126	0·916	1·509

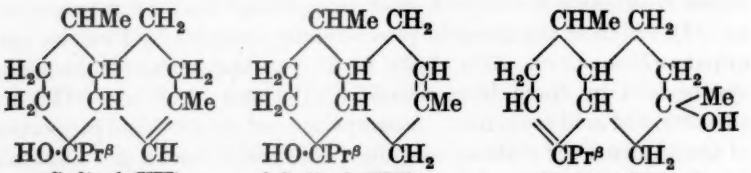
The close similarity of these compounds is evident. Further, they all give liquid addition products with the halogen acids, and by heating with sulphur, a good yield of cadalene. As *iso*cadinene and Ruzicka and Capato's compound are both produced by the prolonged action of acids on the hexahydrocadalene framework, it is probable that (II) represents the end-product to which the hexahydrocadalenes are transformed by the action of acid reagents. The exact position of the double bonds in this molecule, however, is not known with certainty.



These considerations also afford an explanation of Ruzicka and Capato's failure to synthesise cadinene (V and VI) by the continued action of acid reagents upon the nerolidol and bisabolene structures (*loc. cit.*).

B. *Some Dicyclic Alcohols associated with Cadinene.*

It is a remarkable fact that although cadinene is so widely distributed in nature, yet the cadinol alcohols, of which three isomeric forms (VII, VIII, and IX) are obviously possible, have hitherto been discovered in only one plant source, *viz.*, galbanum oil.



Recently, while examining the higher-boiling fractions of oil of false cubebs, we observed that a good yield of cadinene dihydrochloride could be obtained from the alcoholic fraction. The presence of an alcohol of the type VII, VIII, or IX was thus indicated. An extensive fractionation of the oil under diminished pressure revealed the presence of several distinct though closely similar compounds. The rotatory power–b. p. curve for the various fractions showed two distinct breaks, indicating the presence of at least two compounds. Further work led to the isolation of a constant-boiling mixture of isomeric, unsaturated, dicyclic sesquiterpene alcohols, $C_{15}H_{25}(OH)$, the principal constituent of which proved to be a l-*cadinol*, which is identical in all its physical and chemical properties excepting the optical rotation with Semmler's *d*-cadinol from galbanum oil, as the following figures show:

	B. p.	*d*.	n_D.	$[R_L]_D$.	
l-Cadinol	153—155°/10 mm.	0·9727	1·508	68·00	$[\alpha]^{15°}_{5461}$ −54°
d-Cadinol from galbanum oil	155—165/12 mm.	0·9720	1·507	67·97	α_D +22°

From the alcohol fraction of oil of false cubebs we have isolated an apparently new dicyclic *sesquiterpene alcohol*, $C_{15}H_{25}(OH)$, which does not form a stable hydrochloride and therefore cannot be regarded as a cadinene derivative. The new alcohol, for which we propose the name *cubebol*,* is crystalline in a pure state, but owing to its extreme solubility in all ordinary organic solvents and in cadinol it cannot be isolated directly from the oil. We have obtained it in a pure form by the hydrolysis of its *phenylurethane* derivative. This derivative, and the *α-naphthylurethane*, also prepared, should serve definitely to characterise the alcohol. The dicyclic structure of cubebol has been established (*a*) by the formation of a *dibromide*, $C_{15}H_{25}OBr_2{\cdot}CO{\cdot}NH{\cdot}C_6H_5$, from the phenylurethane derivative and (*b*) by the unsaturation of the alcohol itself, which forms an unstable, oily *dibromide*, $C_{15}H_{26}OBr_2$. The quantity of this alcohol so far available has not permitted a more complete examination of its structure, but preliminary experiments indicate that it does not dehydrogenate to either cadalene or eudalene, and therefore does not appear to belong to the hydrated hexahydrocadalene series, as might at first be supposed from its association with cadinol in nature.

Experimental.

Sesquiterpene from Oil of Cade.—This sesquiterpene, isolated as previously described and purified by vacuum distillation, had b. p.

* "Cubeb camphor," described in the early literature, appears to differ from cubebol in its higher m. p., lower solubility, etc.

124—128°/12 mm., $d_4^{20°}$ 0·9181, $n_D^{20°}$ 1·5150, $[R_L]_D$ 67·0 (calc. for a dicyclic sesquiterpene, 66·2). The large exaltation appears to be characteristic of this compound and of *iso*cadinene, and may indicate a system of conjugated bonds (compare II) or, less probably, the admixture of a monocyclic component (compare Semmler and Jakubowicz, *Ber.*, 1914, **47**, 2252) (Found: C, 87·9; H, 11·7. Calc. for $C_{15}H_{24}$: C, 88·2; H, 11·8%).

The sesquiterpene (2·8 g.) was mixed with finely-powdered sulphur (1·2 g.) and heated at 200°; evolution of hydrogen sulphide then began. The temperature was gradually raised to 250° during 1 hour. The product, isolated by vacuum distillation, consisted principally of a mobile oil, b. p. 130—150°/10 mm., which was repeatedly distilled over sodium. This oil gave with a concentrated alcoholic solution of picric acid a good yield of cadalene picrate which, alone or mixed with a specimen prepared from cadalene obtained by the dehydrogenation of pure cadinene, melted at 114°.

iso*Cadinene* was prepared from pure cadinene (regenerated from the dihydrochloride) by the action of glacial acetic acid in sealed tubes at 230—240°. It is difficult to convert cadinene completely by this method into its isomeric form, and the product often contains small amounts of unchanged cadinene which may be removed by conversion into the dihydrochloride.

*iso*Cadinene (2·4 g.) was dehydrogenated by heating with sulphur as described above, and the product identified as cadalene (picrate, m. p. 114°). Yield, 40%.

Fractionation of Oil of False Cubebs.—The oil was fractionally distilled under reduced pressure. The principal sesquiterpene fractions were (*a*) a small fraction, b. p. 116—128°/10 mm., containing a little cadinene; (*b*) a fraction, b. p. 130—148°/10 mm., which gave a good yield of cadinene dihydrochloride when treated with hydrogen chloride in glacial acetic acid solution. The liquid portion of the hydrochloride was regenerated by heating with sodium acetate in glacial acetic acid solution, and the product consisted of a sesquiterpene, b. p. 120—124°/10 mm., which, however, still contained a small quantity of cadinene and resembled fraction (*a*) in its properties. The next fraction (*c*) was alcoholic, b. p. 148—160°/10 mm., and consisted of a bluish-green, viscous liquid. This liquid (120 g.) was hydrolysed by heating with methyl-alcoholic potash (25 g. of KOH in 400 c.c. of alcohol), the alcohol distilled off, water added, and the product extracted with ether and dried. After removal of the ether, the product was redistilled under reduced pressure. The larger part (80 g.) consisted of a bluish-green liquid, b. p. 153—155°/10 mm., $d_4^{16°}$ 0·9727, $n_D^{16°}$ 1·508, $[\alpha]_{5461}^{15°}$ − 54°, $[R_L]_D$ 68·0 (calc. for a dicyclic sesquiterpene alcohol,

68·12) (Found: C, 81·3; H, 11·6. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%). The fraction was unsaturated and gave a 30% yield of cadinene dihydrochloride, m. p. 118°, $[\alpha]_{5461}^{16°}$ − 43·7° in 2·380% chloroform solution, when treated in glacial acetic acid solution with dry hydrogen chloride.

Cubebol Phenylurethane.—The alcohol fraction (20 g.) and phenylcarbimide (10 g.) were heated together for 15 hours at 80—100°. On cooling, diphenylcarbamide, m. p. 238°, crystallised. The dark oily residue, isolated by means of anhydrous ether, in which diphenylcarbamide is nearly insoluble, was dissolved in alcohol, and water added to the point of precipitation. The *phenylurethane*, which slowly crystallised at 0° in well-defined needles, was repeatedly extracted with anhydrous ether and recrystallised from alcohol, in which it was moderately easily soluble; it then melted at 186° and had $[\alpha]_{5461}^{19°}$ + 58·9° in 5% chloroform solution (Found: C, 77·0; H, 9·4; N, 4·4. $C_{22}H_{31}O_2N$ requires C, 77·4; H, 9·2; N, 4·1%). The yield (about 4%) could be somewhat increased by steam-distilling the alcoholic solution after no more crystals would separate from it; the distillate consisted of hydrocarbons and unattacked alcohol and from the residue a further quantity of the phenylurethane could be crystallised.

A *dibromide* was prepared from the phenylurethane by treating an alcoholic solution with excess of bromine at a low temperature. A solid compound separated on the addition of a little water. It was rather unstable, decomposing at 76—80°, and could not be satisfactorily purified owing to the small quantity available (Found: Br, 36·4. $C_{22}H_{31}O_2NBr_2$ requires Br, 32·0%).

Cubebol α-Naphthylurethane.—This was prepared from the cadinol fraction by a method similar to that described above, but it was more difficult to separate from the dinaphthylcarbamide, m. p. 284°, produced. It crystallised from alcohol, in which solvent and in ether it is less soluble than the phenylurethane derivative, as a mass of minute needles, m. p. 197—198·5° (Found: C, 80·7; H, 8·2. $C_{26}H_{33}O_2N$ requires C, 79·8; H, 8·5%).

Cubebol.—The phenylurethane was unattacked by boiling dilute methyl- or ethyl-alcoholic potassium hydroxide, or by acids, but was hydrolysed (1 g.) by heating with ethyl-alcoholic potassium hydroxide (1 g. in 12 c.c.) in sealed tubes for 2—3 hours, finally at 186°. After cooling, the product was diluted with water, neutralised with carbon dioxide, and repeatedly extracted with ether. The ethereal extracts were washed with dilute sulphuric acid (to remove aniline), then with dilute sodium carbonate solution, and dried. On removing the ether, a crystalline product was obtained which was extremely soluble in all ordinary organic

solvents, the vapour of ether or ligroin being sufficient to liquefy it. The substance was purified by vacuum sublimation and had m. p. 61—62° (Found : C, 80·7 ; H, 11·2. $C_{15}H_{26}O$ requires C, 81·1 ; H, 11·7%).

When the alcohol is treated with hydrogen chloride in ethereal or glacial acetic acid solution at 0°, a characteristic red coloration is produced, but no stable hydrochloride is formed ; the product contains less than one atom of chlorine (Found : Cl, 9·6. $C_{15}H_{26}OCl$ requires Cl, 13·7%).

Cubebol Dibromide.—When the alcohol was gradually treated with bromine, both being in chloroform solution at 0°, addition and, to a small extent, substitution took place, accompanied by a deep blue coloration. On removing the chloroform, an unstable oil was obtained, which decomposed very quickly on exposure to light (Found : Br, 42·2. $C_{15}H_{26}OBr_2$ requires Br, 41·8%).

We desire to express grateful thanks to the Carnegie Trust for a scholarship which enabled one of us (J. M. R.) to take part in this investigation, and for a grant in aid of the expenses. To the Chemical Society we are indebted for a grant which defrayed the cost of some of the materials.

UNIVERSITY OF GLASGOW. [*Received, July 1st,* 1926.]

CCCLXXIV.—*The Specific Heats of Hydrocyanic Acid. A Reply.*

By EDITH HILDA INGOLD.

MY original contribution on this subject (J., 1922, **121**, 1604) having been criticised by Partington and Carroll (*Phil. Mag.*, 1925, **49**, 665) on the ground that, in their opinion, my vapour density measurements indicated marked association in the gaseous state, it became necessary to point out (this vol., p. 26) that the argument on which Partington and Carroll based their contention was not in accordance with accepted physico-chemical principles. In reply, Partington (this vol., p. 1559) abandons the former method of calculation (or at least does not refer to it) and adopts a new one, my vapour density measurements being now compared with numbers calculated from Bredig and Teichmann's critical data (*Z. Elektrochem.*, 1925, **31**, 499).

That considerable uncertainty surrounds all such calculations *

* This is also true of the numerical comparisons contained in the first paragraph of Partington's paper, which involve both temperature and pressure extrapolations in the case of a vapour not far removed from liquefaction.

is illustrated by Menzies's elaborate investigation of the case of water vapour (*J. Amer. Chem. Soc.*, 1921, **43**, 851) for which comparatively extensive experimental data are available, and in the case of hydrocyanic acid the uncertainty is particularly great for reasons which have already more than once been pointed out (Partington and Carroll, *loc. cit.*; Ingold, *loc. cit.*). But even taking the calculated numbers as they stand, the excess of the observed over the calculated density, assumed to represent the association, varies almost equally on either side of zero (up to $\pm$ 0·7%) if the value for 65° be excluded from the series. Whether this isolated discrepancy (the difference is nearly 2%) is due to experimental or theoretical inaccuracies, as may well be the case, or whether it represents evidence of association, as Partington claims (contrary to analogy), matters not in the slightest, since Partington and Carroll's criticism would remain valid only if association were proved to occur throughout the whole temperature range over which the specific-heat ratio was measured.

In the "Summary" at the end of the paper Partington's conclusions are set forth as follows: "It is shown that the reasons advanced against the assumption of Partington and Carroll that hydrogen cyanide vapour is associated to a small * extent at room temperature are inconclusive." This statement is misleading in several particulars. First, Partington and Carroll's "assumption" of association was *not confined to room temperature*, but included higher temperatures: otherwise there would have been no point in their discussing my experiments, which were conducted between 65° and 210°, the upper part of the range being the more important. Secondly, the vapour density of hydrocyanic acid has not yet been determined at room temperature; and, naturally, I did not "advance reasons against" any assumption which Partington and Carroll might have made relating to a temperature for which no data exist. The implied restriction of Partington and Carroll's "assumption of association" to a temperature for which it cannot at present be tested, and which, in any case, is outside my experimental range, represents a welcome modification of the position previously adopted. It remains to be added, in connexion with the stress laid by Partington on the probable association of hydrocyanic acid in the liquid state, that I had already drawn an analogy between this substance and water, which is strongly associated in the liquid state and yet has been shown by Menzies (*loc. cit.*) to yield an unassociated vapour.

THE UNIVERSITY, LEEDS. [*Received, July 5th*, 1926.]

* Actually, associations to the extent of 13% were contemplated.

CCCLXXV.—*The Metallic Compounds of Certain Monoximes and the Structure of the Oximes.*

By THOMAS WESTON JOHNS TAYLOR and (MISS) ELINOR KATHARINE EWBANK.

THAT certain oximes will form stable compounds with metals has long been known and indications exist that the power of forming such compounds is determined by the constitution and configuration of the oxime; for example, Tschugaev (*Z. anorg. Chem.*, 1905, **46**, 148) has shown that α-benzildioxime will form complexes with heavy metals, whereas the β-dioxime will not. The question of configuration and constitution necessary in an oxime for metallic complex formation has also been partly investigated by Whiteley (J., 1903, **83**, 24) and Ponzio (*Gazzetta*, 1922, **52**, i, 285), but no generalisation has been put forward which attempts to explain the experimental results.

The interest attaching to the oximes led us to investigate eleven monoximes of different types and the possibility of obtaining from them complexes with iron, nickel, cobalt, or copper. The results are in Table I; the following points will be noticed.

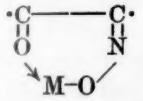
(i) The oximes investigated fall into two classes, those forming metallic complexes and giving a characteristic blue colour with alkaline solutions of ferrous salts, and those that do not; the only doubtful case is methyl α-oximinoethyl ketone, which gives no complexes but shows the characteristic blue colour.

(ii) Of the metals used, cobalt forms complexes with greater facility than the others.

(iii) Nickel complexes could be obtained from oximinoacetylacetone and ethyl oximinoacetoacetate only in the presence of ammonia, and ammonia residues are contained in the resulting complex.

The structure of the metallic complexes formed by oximinoketones, -esters or -amides, to which classes the oximes investigated belong, is almost certainly

(I.)



where the arrow represents a co-ordinate link formed by two electrons from the oxygen atom; this structure explains the non-salt-like properties of the complexes, and also their actual formulæ, as, for example, Tschugaev's compound of cobalt and α-benzilmonoxime, $Co(Ph{\cdot}CO{\cdot}CPh{:}NO)_3$, where the typical co-ordination number of cobalt, six, can be recognised.

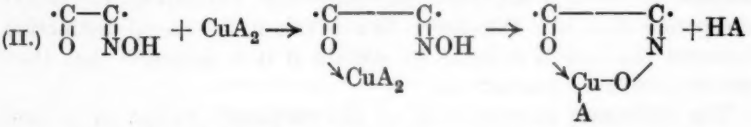
TABLE I.

In cols. 2, 3, 4, and 5 are the formulæ of the metallic complexes obtained; R represents a molecule of the oxime minus a hydrogen atom. Compounds marked with a query are those which it was difficult to obtain analytically pure or those whose formula is doubtful for some other reason (see experimental section).

Oxime.	Fe.	Co.	Ni.	Cu.
$Me\cdot CO\cdot CH{:}NOH$.	Blue col. Sol. in benzene.	?R_2Co.	?R_2Ni.	Indeterminate.
$Me\cdot CO\cdot C(:NOH)\cdot COMe$.	,,	R_2Co.	[$Me\cdot C(:NH)\cdot C(:N\cdot O\cdot)\cdot COMe]_2Ni$.	?$R\cdot Cu\cdot O\cdot CO\cdot CH_3,H_2O$.
$Ph\cdot CO\cdot C(:NOH)\cdot COMe$.	,,	R_2Co.	Nil.	$R\cdot CuOH$.
$Me\cdot CO\cdot C(:NOH)\cdot CO_2Et$.	,,	R_2Co.	[$Me\cdot C(:NH)\cdot C(:N\cdot O\cdot)\cdot CO_2Et]_2Ni$.	$R\cdot CuOH,H_2O$ and $R\cdot CuOH$.
$Ph\cdot CO\cdot CH{:}NOH$.	R_2Fe.	R_2Co.	Indeterminate.	Nil.
$OH\cdot N{:}C(CO\cdot NHPh)_2$.	R_2Fe.*	?R_2Co.	R_2Ni.	R_2Cu.
$Ph\cdot CO\cdot CPh{:}NOH(\alpha)$.	Blue col. Sol. in benzene.	R_2Co.†	Indeterminate.	$R\cdot CuOH$.
$Me\cdot CO\cdot CMe{:}NOH$.	,,	Nil.	Nil.	Nil.
$Ph\cdot CO\cdot C(:NOH)\cdot CO_2Et$.	No blue col.	,,	,,	,,
$OH\cdot N{:}C(CO_2Et)_2$.	,,	,,	,,	,,
$Ph\cdot CO\cdot CPh{:}NOH(\beta)$.	,,	,,	,,	,,

* Whiteley, *loc. cit.* † Tschugaev, *J. pr. Chem.*, 1907, **76**, 88.

The view that leads to the most consistent explanation of the results in Table I is that, in oximes of the classes investigated, formation of metallic complexes is determined by the presence of a reactive carbonyl group: oximinoacetylacetone forms complexes, but ethyl oximinomalonate does not; α-benzilmonoxime, which forms complexes, contains a reactive carbonyl group, whereas that in the β-oxime, which forms no complexes, is less reactive. That the presence of such a group should be the determining factor is easily comprehensible if it is assumed that the mechanism of metallic complex formation is not formation of the true metallic salt of the oxime followed by closure of the co-ordinated ring, but an initial formation of a co-ordinate link between the reactive carbonyl group and the metallic ion or salt followed by ring closure through elimination of a hydrogen ion or a molecule of the acid originally united with the metal—a scheme shown in (II).

(II.) 

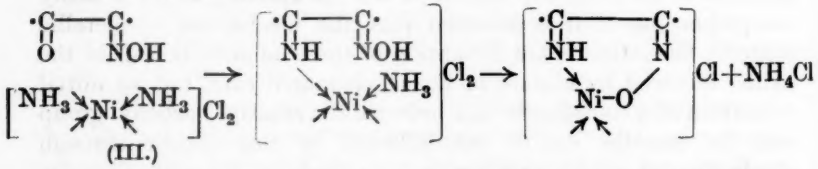
In a complex such as R_3Co the process occurs three times, and if no sufficiently reactive carbonyl group is present the initial step cannot take place and no complex can result.

The view receives some support from the work of Feigl and Rubinstein (*Annalen*, 1923, **433**, 183), who isolated and analysed a co-ordination compound $[Co(DH_2)_2]Cl_2$ (DH_2 = dimethylglyoxime) formed from dimethylglyoxime and cobaltous chloride; this is

evidence that union can take place between an analogous compound and a cobalt salt without preliminary elimination of the anion united with the cobalt.

It may be objected to this view that the work of Hieber (*Ber.*, 1921, **54**, 902) shows that, in a keto-enol tautomeride, the enol alone forms complexes, at least with copper, and that the enolic form of a compound such as ethyl acetoacetate contains no reactive carbonyl group. It is highly probable, however, that the two reactions are dissimilar: ethyl acetoacetate forms with cobalt and nickel under the conditions which are sufficient for the oximes, not simple complexes but compounds of unknown constitution, $Ni_2C_{20}H_{32}O_{11}$ and $Co_2C_{20}H_{30}O_{11}$ (Wislicenus and Stoeber, *Ber.*, 1902, **35**, 546); and its copper compound has no analogy with those of the oximes investigated, with the exception of oximinomalonanilide, which stands apart from the other oximes in possessing a mobile hydrogen atom and is in this comparable with ethyl acetoacetate.

In the nickel complexes which require ammonia for their formation and contain ammonia residues it is probable that the primary step is reaction between the carbonyl group and the ammonia–nickel complex present in the ammoniacal solution. As can be seen in Table I, nickel–oxime complexes are rare; this suggests that a carbonyl group is incapable of forming a stable co-ordinate link with nickel, but that in some cases it can react with the nickel ammine complex to give the necessary first step and thus the ammonia-containing complex (III).

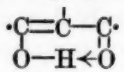


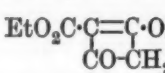
(III.)

No explanation is offered for the failure of ethyl oximinobenzoylacetate to form complexes, although the corresponding acetyl compound does so. Whatever view is taken, the sharp distinction between the two is difficult to explain if it is assumed that they possess similar constitutions.

The difference in reactivity of the carbonyl groups in α- and β-benzilmonoximes already referred to may possibly arise from purely steric causes, the proximity of the hydroxyl group affecting the reactivity of the carbonyl group in the β-oxime but not that in the α-oxime. A much more probable explanation is, however, that in α-oximino-ketones and similarly constituted compounds the stereoisomeride which contains the less reactive carbonyl group itself possesses a six-membered co-ordinated ring structure.

Sidgwick (J., 1925, **127**, 907) has pointed out that the physical properties of the enolic form of a β-diketone or ketonic ester can be accounted for only by assigning to the enol the structure (IV).

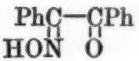
(IV.) 

 (V.)

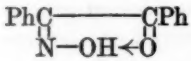
Further strong evidence for his view is afforded by the chemical properties of ethyl *cyclo*butenolonecarboxylate (V) (Schroeter, *Ber.*, 1916, **49**, 2714; see also Dieckmann and Wittmann, *Ber.*, 1922, **55**, 3331), which, although in many ways constituted identically with the enolic form of a β-ketonic ester, differs from such enols in being an acid strong enough to decompose carbonates. Co-ordination between the enolic hydrogen atom and a carbonyl group is obviously not present in this compound, and this can be ascribed to the presence of the four-membered ring; for co-ordination would mean the formation of the ring system (VI), a system which is very rare, if, indeed, it occurs at all.

In the α-oximino-ketones similar six-membered co-ordinated rings can occur, and the properties of the benzilmonoximes [α-benzilmonoxime, m. p. 137·8°, is sparingly soluble in benzene or carbon disulphide and reacts with aniline in the cold in 8 days and with phenylhydrazine at 30–40° (von Auwers and V. Meyer, *Ber.*, 1889, **22**, 540); β-benzilmonoxime, m. p. 113—114°, is easily soluble in all organic solvents and does not react with aniline and phenylhydrazine under the conditions stated (von Auwers and Siegfeld, *Ber.*, 1893, **26**, 794)] indicate that these have the structures (VII) and (VIII).

(VI.)



(VII; α.)

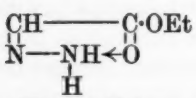


(VIII; β.)

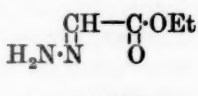
This view not only accounts satisfactorily for the chemical reactivity of these oximes but implies a stereochemical configuration, for it implies that the configuration about the >C:N group is favourable in the β-oxime and unfavourable in the α-oxime to the formation of the co-ordinated ring. The configurations so arrived at are those deduced by Meisenheimer from the oxidation product of triphenyl*iso*oxazole (*Ber.*, 1921, **54**, 3208).

This view of the difference in reactivity between the benzilmonoximes and the deduction of stereochemical configurations from it receive support from the recorded properties of the stereoisomeric hydrazones of camphorquinone (Forster and Zimmerli, J., 1910, **97**, 2156) and of glyoxylic ester (Staudinger, Hammet, and Siegwart, *Helv. Chim. Acta*, 1921, **4**, 228), where the striking difference

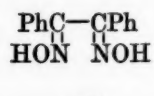
in reactivity of the isomerides clearly points to the presence of a co-ordinated ring in one isomeride and its absence in the other. In the latter case, one isomeride, the liquid, is more volatile and less soluble in water than the other, and reacts only slowly with phenylcarbimide and not at all with diphenylketen; its molecular weight in benzene is normal: the other, the solid, is associated in solution and reacts readily with both reagents. Here the structures must be those shown in (IX) and (X), and the stereochemical configurations follow.



(IX; liquid form.)



(X; solid form.)



(XI.)

The benzildioximes deserve some mention: the α-dioxime forms a nickel complex, R_2Ni, and the β-dioxime forms no metallic complexes (Tschugaev, *loc. cit.*). If the initial step in complex formation is co-ordination of the metal with one of the tervalent nitrogen atoms, the α-dioxime should have a configuration such that there is less possibility of the dioxime itself possessing a co-ordinated structure; it should be represented by (XI), which is the configuration assigned to it by Meisenheimer (*loc. cit.*). The γ-dioxime forms a nickel complex (Atack, J., 1913, **103**, 1317), but it is of quite different constitution from that of the α-dioxime and cannot be formed by a reaction of mechanism similar to that outlined above.

Experimental.

The blue colour produced in the presence of ferrous iron (Table I) was observed on shaking the oxime with aqueous ferrous sulphate and adding dilute caustic soda solution. In all cases, on shaking with benzene, the colour passed into the benzene; all the colorations were destroyed on heating, except that given by oximinoacetylacetone.

Iron was estimated as ferric oxide, and cobalt as the sulphate. The nickel compounds were very explosive if heated in a crucible with nitric acid; they were decomposed by heating in a glass tube in a stream of oxygen; the residue of nickel oxide and some metallic nickel, probably produced by the decomposition of nickel carbonyl, was treated with nitric acid and weighed as nickel oxide. Copper was estimated iodometrically after the complex had been treated with nitric and sulphuric acids.

Oximinoacetone was prepared from ethyl acetoacetate by Ceresole's modification of Meyer and Zublin's method (Charrier, *Centr.*, 1907, II, 1231). No compounds were obtained on treatment with a

solution of cobalt or nickel acetate or on the further addition of ammonia. Ill-defined compounds were obtained, if caustic soda was present, after 1 hour's heating or a fortnight's keeping (Found: Ni, 26·4. R_2Ni requires Ni, 25·4%. Found: Co, 26·1, 24·6, 26·2. R_2Co requires Co, 25·5%). No conclusive results were obtained with copper acetate, although there were indications of the formation of an unstable complex.

Oximinoacetylacetone (Wolff, *Annalen*, 1902, **325**, 139) (1·3 to 3 mols.) in warm aqueous solution was mixed with aqueous cobalt acetate (1 mol.). The reddish-orange precipitate was washed with water and cold alcohol (Found: Co, 13·2, 13·3; *M*, in benzene, 406. R_3Co requires Co, 13·3%; *M*, 443). The complex is readily soluble in benzene and soluble in alcohol. Ponzio (*loc. cit.*) obtained a compound R_2Co by this method.

An alcoholic solution of the oxime, on mixing with an aqueous ammoniacal solution of nickel acetate, gave a green precipitate, rapidly changing to reddish-brown. This was digested with hot water and alcohol; its structure is most probably

$$[CH_3{\cdot}C(:NH){\cdot}C(CO{\cdot}CH_3):N{\cdot}O{\cdot}]_2Ni$$

(Found: C, 38·3; H, 4·5; N, 17·5; Ni, 19·0; *M*, in naphthalene, 305. Calc.: C, 38·4; H, 4·5; N, 17·9; Ni, 18·8%; *M*, 310). The initial green precipitate contains 23·0% of Ni and is probably $CH_3{\cdot}C(:NH){\cdot}C(CO{\cdot}CH_3):N{\cdot}O{\cdot}Ni{\cdot}O{\cdot}CO{\cdot}CH_3$ (Calc.: Ni, 23·1%).

The oxime and copper acetate (1 or 0·5 mol.) in aqueous solution gave a green compound (Found: Cu, 24·0, 24·3%), probably

$$R{\cdot}Cu{\cdot}O{\cdot}CO{\cdot}CH_3,H_2O,$$

(Calc.: Cu, 23·7%); it decomposed on heating. Ponzio's olive-green compound R_2Cu could not be prepared by the above procedure.

Oximinobenzoylacetone (Wolff, *loc. cit.*). Addition of aqueous cobalt acetate (1 mol.) to an alcoholic solution of the oxime (2 or 3 mols.) gave in the presence of a little ammonia a yellow compound, which was digested with hot water and alcohol (Found: C, 57·0; H, 4·1; N, 6·8; Co, 9·4, 9·35; *M*, in benzene, 540. R_3Co requires C, 57·2; H, 3·8; N, 6·7; Co, 9·4%; *M*, 629). Here again Ponzio describes a cobaltous compound. No complex could be obtained containing nickel, but with an aqueous solution of copper acetate the oxime gave a green precipitate, which was digested with hot alcohol (Found: Cu, 23·2, 23·4. R·CuOH requires Cu, 23·5%).

Ethyl oximinoacetoacetate (Boulanger, *Bull. Soc. chim.*, 1905, **33**, 560), dissolved in dilute ammonia and mixed with aqueous cobalt acetate, gave a rather unstable, red compound, which was washed with cold water (it is decomposed by hot water) (Found: Co, 11·8, 11·6; *M*, in benzene, 530, 553. R_3Co requires Co, 11·1%; *M*, 533).

With nickel acetate in aqueous solution the oxime gave on addition of ammonia, followed by boiling, a yellow complex containing ammonia. The yield corresponded to one-fifth of the oxime taken, the remainder being recovered unchanged. The complex is probably similar in structure to that obtained from oximinoacetylacetone (Found: C, 38·5; H, 4·7; N, 14·7; Ni, 15·9; *M*, in nitrobenzene, 386. Calc.: C, 38·65; H, 4·8; N, 15·0; Ni, 15·7%; *M*, 373). It is decomposed by dilute sulphuric acid and is somewhat soluble in alcohol and in aqueous ammonia.

An alcoholic solution of the oxime gave with aqueous copper acetate a green precipitate, which was washed with hot water and alcohol (Found: Cu, 24·7, 24·5, 24·4; H_2O, 7·1. $R{\cdot}Cu{\cdot}OH,H_2O$ requires Cu, 24·7; H_2O, 7·0%). On drying at 85—90° or in a desiccator the anhydrous compound, which is hygroscopic, was obtained (Found: Cu, 26·8, 26·1. Calc.: Cu, 26·5%). The compound explodes at 100—110° and is insoluble in naphthalene, benzene, and tetrahydronaphthalene.

Oximinoacetophenone (Claisen, *Ber.*, 1887, **20**, 2194). In aqueous solution with ferrous sulphate and ammonium acetate a stable, blue precipitate was formed which was purified as before and dried at 60° (Found: C, 54·2; H, 3·6; N, 7·6; Fe, 16·15, 15·9. R_2Fe requires C, 54·6; H, 3·5; N, 8·0; Fe, 15·9%). The compound is hygroscopic and is insoluble in benzene; it appears to decompose when dissolved in molten naphthalene.

The oxime (3 mols.) and cobalt acetate (1 mol.) in aqueous solution gave a third of the theoretical yield of a brownish-yellow precipitate, which, after washing, was dried at 100° (Found: C, 57·6; H, 3·8; N, 8·0, 7·8; Co, 11·85, 11·4; *M*, in nitrobenzene, 534. R_3Co requires C, 57·25; H, 3·6; N, 8·35; Co, 11·7%; *M*, 503). If the proportion of oxime to salt is 2 : 1, indeterminate compounds containing a higher percentage of cobalt are obtained.

With aqueous solutions of nickel acetate, indeterminate, dull green compounds were obtained, very soluble in alcohol and only slightly soluble in benzene. They are much more explosive than any of the other nickel compounds and are best decomposed by heating them in a stream of air. They char below 100° and possibly have the constitution $R{\cdot}Ni{\cdot}O{\cdot}CO{\cdot}CH_3$.

Oximinomalonanilide (Whiteley, *loc. cit.*). The compound R_2Fe (Whiteley, *loc. cit.*) was prepared (Found: C, 57·6; H, 3·9; N, 13·4; Fe, 9·2, 9·05. Calc.: C, 58·1; H, 3·9; N, 13·55; Fe, 9·0%). The complex is insoluble in benzene.

Compounds with cobalt (i; R_2Co, buff), nickel (ii; R_2Ni, buff), and copper (iii; R_2Cu, green) were obtained from the corresponding acetates and washed with hot water and alcohol [Found (i): C,

57·8; H, 4·1; N, 13·4; Co, 9·55, 9·5. Calc.: C, 57·8; H, 3·85; N, 13·5; Co, 9·5%. Found (ii): C, 57·4; H, 4·0; N, 12·9; Ni, 9·5, 9·15. Calc.: C, 57·8; H, 3·8; N, 13·5; Ni, 9·4%. Found (iii): C, 57·1; H, 3·95; N, 13·1; Cu, 10·0, 10·2. Calc.: C, 57·4; H, 3·8; N, 13·4; Cu, 10·1%]. Molecular-weight determinations were untrustworthy because of the small solubility of the compounds in suitable solvents; in naphthalene, in which they dissolve slowly at 150—200°, the cobalt compound showed a molecular weight roughly double that required for R_2Co, and the nickel compound one of 589 (calc. for R_2Ni, 620).

α-Benzilmonoxime (von Auwers and Siegfeld, *Ber.*, 1893, **26**, 791). The cobalt compound has been described by Tschugaev (*loc. cit.*) and Ponzio; it can be obtained in better yield by adding a little ammonia to the solution. Its molecular weight in nitrobenzene is 690 (calc., 731). With nickel acetate in the presence of excess caustic potash, indefinite, green compounds were obtained containing from 14·2 to 16·6% of the metal; they were soluble in pyridine, benzene and tetrahydronaphthalene, but not in alcohol. The oxime in alcohol gave with aqueous copper acetate a green precipitate containing 21·2% of Cu (calc. for R·CuOH, 20·9%).

Methyl α-oximinoethyl ketone (Diels and Jost, *Ber.*, 1902, **35**, 3292). No definite compounds with the metals investigated could be obtained, although there were indications of complex formation with copper.

Ethyloximinobenzoylacetate (Wolff, *Ber.*, 1903, **36**, 3614). No blue colour with alkaline ferrous solution was observed—a result in disagreement with that of Whiteley (*loc. cit.*), but it is possible that her sample was contaminated with oximinoacetophenone, since it was prepared by Perkin's method (J., 1885, **47**, 244).

Ethyloximinomalonate was prepared by Bouveault and Wahl's method (*Bull. Soc. chim.*, 1903, **29**, 961).

β-Benzilmonoxime was prepared by the method of von Auwers and Siegfeld (*loc. cit.*). No indications could be found of metallic complex formation with any of the last three oximes.

In conclusion, the authors desire to express their sincere thanks to Mr. J. J. Manley for his valuable advice on analytical methods.

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CCCLXXVI.—*Preparation of the 5-Halogeno-resorcinols.*

By Herbert Henry Hodgson and John Samuel Wignall.

The three 5-halogenoresorcinols have been prepared by converting the 3-halogeno-5-amino-anisoles (this vol., p. 2078) into the 5-halogeno-3-hydroxyanisoles and hydrolysing these.

5-Halogeno-3-hydroxyanisoles.—The 3-halogeno-5-aminoanisole (14 g.) or its sulphate (20 g.) in a mixture of sulphuric acid (15 g.) and water (150 c.c.) was diazotised at 0·5°, the excess of nitrous acid destroyed by carbamide, and the clear solution added gradually to a vigorously boiling mixture of sulphuric acid (120 g.) and water (150 c.c.) through which a current of steam was passing. The 5-halogeno-3-hydroxyanisole was only slowly volatilised. The voluminous distillate was made just alkaline, concentrated to small bulk, and acidified; the product then separated as an oil which solidified.

The 5-halogeno-3-hydroxyanisoles all reduce boiling Fehling's solution very slowly, and in aqueous solution give a faint bluish-pink coloration with ferric chloride.

5-Chloro-3-hydroxyanisole is readily soluble in water, alcohol, benzene, or glacial acetic acid, and crystallises from light petroleum or water in colourless needles, m. p. 99° (Found: Cl, 22·45. $C_7H_7O_2Cl$ requires Cl, 22·4%). *5-Chloro-2 : 4 : 6-tribromo-3-hydroxyanisole* is obtained from glacial acetic acid in colourless needles, m. p. 110° (0·0884 g. gave 0·1574 g. of silver halides. Calc., 0·1581 g.), and *5-bromo-3-hydroxyanisole* from water in colourless needles, m. p. 102° (Found: Br, 39·2. $C_7H_7O_2Br$ requires Br, 39·4%); the latter is less readily soluble in water than the chloro-analogue. *2 : 4 : 5 : 6-Tetrabromo-3-hydroxyanisole* crystallises from glacial acetic acid in colourless needles, m. p. 120° (Found: Br, 72·5. $C_7H_4O_2Br_4$ requires Br, 72·7%). *5-Iodo-3-hydroxyanisole* sublimes in colourless needles, m. p. 90° (Found: I, 50·7. $C_7H_7O_2I$ requires I, 50·8%). It is almost insoluble in water or light petroleum, but dissolves readily in alcohol or benzene. *2 : 4 : 6-Tribromo-5-iodo-3-hydroxyanisole* crystallises from dilute acetic acid in colourless needles, m. p. 125° (0·0991 g. gave 0·1621 g. of silver halides. Calc., 0·1626 g.).

5-Halogenoresorcinols.—The 5-halogeno-3-hydroxyanisole (7 g.) was boiled under reflux for 3 hours with hydriodic acid (60 c.c.; *d* 1·6), the solution decolorised by addition of sodium thiosulphate, and the 4-halogenoresorcinol extracted with ether. The product was stirred in cold 5% aqueous sodium hydroxide (80 c.c.)

to remove sulphur and recovered by acidification and extraction with ether (yields, 5—6 g.).

The 5-halogenoresorcinols all reduce boiling Fehling's solution and give pronounced bluish-purple colorations with ferric chloride. 5-Chloro- and 5-iodo-resorcinols differ from 5-bromoresorcinol in that their monohydrates are much more stable.

5-Chlororesorcinol.—The crude product from the foregoing hydrolysis crystallised from benzene in colourless needles, m. p. 67°, of the monohydrate (Found: Cl, 21·5. $C_6H_5O_2Cl,H_2O$ requires Cl, 21·8%). When this was sublimed in a vacuum, microcrystalline needles of the anhydrous substance were obtained, m. p. 117° (Found: Cl, 24·4. $C_6H_5O_2Cl$ requires Cl, 24·5%). The anhydrous substance is readily soluble in all the usual solvents except light petroleum, in which it is insoluble, and rapidly absorbs water, regenerating the hydrate (Found: loss in a vacuum over concentrated sulphuric acid, 10·8. Calc.: H_2O, 11·1%). *5-Chloro-2 : 4 : 6-tribromoresorcinol* crystallises from glacial acetic acid or dilute alcohol in colourless needles, m. p. 143° (0·1539 g. gave 0·2762 g. of silver halides. Calc., 0·2851 g.). The low m. p. and the poor analytical result probably indicate the presence of a hydrate. *5-Bromoresorcinol* crystallises from benzene in colourless needles, m. p. 87° (Found: Br, 42·4. $C_6H_5O_2Br$ requires Br, 42·3%). These remain unchanged in m. p. after sublimation in a vacuum, but on recrystallisation from water large prisms of the monohydrate, m. p. about 79°, are obtained (Found: Br, 39·2. Calc. for monohydrate: Br, 38·6%). 2 : 4 : 5 : 6-Tetrabromoresorcinol crystallises from glacial acetic acid or dilute alcohol in colourless needles, m. p. 212° (Claassen, *Ber.*, 1878, **11**, 1440, gives m. p. 163°; Benedikt, *Monatsh.*, 1880, **1**, 366, gives m. p. 167°) (Found: Br, 75·0. Calc.: Br, 75·1%). *5-Iodoresorcinol* crystallises from benzene in colourless needles, m. p. 92·3° (Found: I, 49·9. $C_6H_5O_2I,H_2O$ requires I, 50·0%). On sublimation in a vacuum, colourless needles were obtained which still retained water but melted at 105—113° (Found: I, 52·0. $C_6H_5O_2I$ requires I, 53·8%). Keeping over concentrated sulphuric acid or crystallisation from dry benzene in presence of phosphorus pentoxide failed to dehydrate the product completely. *2 : 4 : 6-Tribromo-5-iodoresorcinol* separates from glacial acetic acid in colourless needles, m. p. 214° (0·0793 g. gave 0·1339 g. of silver halides. Calc., 0·1340 g.).

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 14th*, 1926.]

CCCLXXVII.—*Germanium. Part III. Salts of Germanic Acid.*

By WILLIAM PUGH.

IT is well known that germanium dioxide is soluble both in acids and in alkalis (Winkler, *J. pr. Chem.*, 1886, **34**, 177; van Bemmelen, *Rec. trav. chim.*, 1887, **6**, 205), but whilst a considerable amount of information has been published recently on the salts of germanium dioxide with acids, chiefly by Dennis and his co-workers (*J. Amer. Chem. Soc.*, 1921—1925), comparatively little is known about its salts with bases. The preparation and some of the characteristics of the germanates of sodium, potassium, lithium, barium, lead, and silver are now described.

Sodium Germanate.—In common with other weakly acidic oxides (*e.g.*, silica and tin dioxide) germanium dioxide displaces carbon dioxide from sodium carbonate at its melting point. Pure anhydrous sodium carbonate (0·4884 g.; 1 mol.) and germanium dioxide (0·4819 g.; 1 mol.) were fused together in a platinum crucible over a blast lamp; vigorous effervescence of carbon dioxide occurred and the melt gradually became more viscous. After 5 minutes the melt had become homogeneous and the loss in weight was 0·2025 g. (Calc. for $Na_2CO_3 + GeO_2 = Na_2GeO_3 + CO_2$: 0·2028 g.). By the use of an excess of sodium carbonate only 1½ equivalents of carbon dioxide could be displaced, with the formation of the orthogermanate. Sodium carbonate itself loses carbon dioxide at its melting point; according to Mallard (*Ann. Chim.*, 1873, **28**, 86), the loss is 1·75% of the total weight. Table I gives the observed loss in weight with time of fusion of a mixture of sodium carbonate (0·7495 g.; 2 mols.) and germanium dioxide (0·3695 g.; 1 mol.). The data for sodium carbonate alone (0·9200 g.) are added for comparison. Col. *a* gives the loss in weight in grams, col. *b* that in mols. of carbon dioxide per mol. of sodium carbonate, and col. *c* the loss in mols. of carbon dioxide per mol. of germanium dioxide.

TABLE I.

Time (mins.).	$Na_2CO_3 + GeO_2$.			Na_2CO_3.	
	a.	*b.*	*c.*	*a.*	*b.*
2	0·2060	0·662	1·324	0·0130	0·0340
4	0·2100	0·675	1·350	0·0130	0·0340
7	0·2110	0·678	1·356	0·0135	0·0353
15	0·2120	0·681	1·362	0·0145	0·0379
25	0·2130	0·684	1·368	0·0160	0·0418

These figures show that the mixture loses two-thirds of its carbon dioxide immediately on fusion and that the subsequent loss is small

and comparable with the loss sustained by sodium carbonate when heated alone. There is therefore a clear indication that 4 mols. of carbon dioxide are displaced by 3 mols. of germanium dioxide. The composition of the product corresponds either to a true compound of the formula $4Na_2O,3GeO_2$ or to a mixture of the ortho- and meta-germanates in the proportion 1 : 2. It is significant that Niggli (*J. Amer. Chem. Soc.*, 1913, **35**, 1693) and Morey (*ibid.*, 1914, **36**, 215) have shown that in the system Na_2O–SiO_2 the only stable silicates are the ortho- and the meta-silicates.

Sodium metagermanate, prepared by fusing molecular proportions of sodium carbonate and germanium dioxide, is a white, crystalline substance which is very hygroscopic and absorbs carbon dioxide from the air. It is very soluble, but the solution, which has an intensely alkaline reaction, is rapidly hydrolysed and hydrated germanium dioxide separates. When this solution is evaporated in an atmosphere free from carbon dioxide, it thickens to the consistency of water-glass without crystallising. This viscous solution is highly supersaturated, for on the introduction of a minute nucleus it solidifies completely with evolution of much heat. If, however, the solution be inoculated as it evaporates at the ordinary temperature, the heptahydrate crystallises readily. The best method of preparing this hydrate consists in fusing germanium dioxide with about 10% more than the theoretical quantity of sodium hydroxide, extracting the melt with water, and evaporating the solution over concentrated sulphuric acid. Fusion proceeds much more readily in this case than in the former and, moreover, the excess of sodium hydroxide prevents the undesirable separation of germanium dioxide as the solution becomes concentrated. The crystals were washed with ice-cold water and dried on filter-paper in the air (Found: Na_2O, 21·2; GeO_2, 35·7; H_2O, 43·0. $Na_2GeO_3,7H_2O$ requires Na_2O, 21·2; GeO_2, 35·7; H_2O, 43·1%).

The heptahydrate crystallises from water in the rhombic system. Its complete crystallography is being investigated. On standing in air the crystals lose their transparency owing to the absorption of carbon dioxide, but in its absence they retain their transparency indefinitely. They do not absorb moisture from the air, neither do they effloresce. The aqueous vapour pressure, as determined with a tensimeter, is 4 mm. at 20° and 5·5 mm. at 25°. The crystals melt in their own water of crystallisation at about 83°. When freshly prepared, the heptahydrate dissolves completely in water, the solution being strongly alkaline, but the partly dehydrated or carbonated hydrate does not dissolve completely. Its solubility, expressed in g. of anhydrous sodium germanate per 100 g. of water, is 14 at 0° and 25·9 at 25°. Owing to the weakness of germanic

acid, this salt gives excellent results on direct titration with *N*- or *N*/10-sulphuric acid and a suitable indicator: with methyl-orange the end-point is sharply defined, but with phenolphthalein the pink colour fades gradually and disappears long before the true end-point is reached.

Potassium Germanate.—All attempts to prepare potassium germanate in the wet way have failed. In one experiment 10 g. of germanium dioxide were fused with 14 g. of potassium hydroxide and the melt was extracted with water and filtered. The solution was concentrated over a free flame and finally over concentrated sulphuric acid. A small nucleus of fused potassium germanate was added from time to time, but the solution merely dried to a thick syrup. In another experiment, the solution obtained after extracting the melt with water was poured into alcohol; the liquid slowly separated into two layers. The denser solution of potassium germanate was repeatedly shaken with absolute alcohol in order to remove the excess of potash and then a small nucleus was added, but even on standing over phosphoric oxide it merely dried to a gummy mass. Both these methods can be used for the preparation of the sodium salt, the heptahydrate being obtained in each case. It appears, therefore, that potassium germanate is too soluble to be crystallised from solution.

Not much better success attended the fusion of germanium dioxide with potassium carbonate: observations were made of the rate of displacement of carbon dioxide. The results are in Table II for an equimolecular mixture of potassium carbonate (0·8438 g.) and germanium dioxide (0·6390 g.), fusion being carried out at the temperature of a Méker burner.

TABLE II.

Time (mins.).	Loss in wt. (g.).	Ratio $CO_2 : GeO_2$.
3	0·2002	0·745
5	0·2076	0·772
13	0·2292	0·855
26	0·2362	0·878
60	0·2366	0·879

These results show that germanium dioxide displaces 0·75 equiv. of carbon dioxide immediately on fusion, whilst the remainder of the carbon dioxide is only slowly displaced on prolonged fusion. It is conceivable that the whole of the carbon dioxide would be displaced at a higher temperature. Potassium carbonate when heated alone under the same conditions loses only 0·25% of its weight. Niggli (*loc. cit.*) has shown that in the system K_2O–SiO_2 the only stable silicates are the meta- and the di-silicate, and that when potassium carbonate is fused with silica the following equi-

librium is set up: $K_2Si_2O_5 + K_2CO_3 \rightleftharpoons 2K_2SiO_3 + CO_2$. From a consideration of the results in Table II, it appears that the system K_2O–GeO_2 is analogous. In order to elucidate the constitution of the fused germanates of sodium and potassium further work is necessary under definite conditions of temperature and pressure.

Lithium Germanate.—Lithium metagermanate is readily obtained, as in the case of the sodium salt, by fusing together molar proportions of lithium carbonate and germanium dioxide. The displacement of carbon dioxide is quantitative. Lithium orthogermanate is also obtained, just as readily, by fusing 2 mols. of lithium carbonate with 1 mol. of germanium dioxide. This again brings germanium dioxide into line with silica, for corresponding silicates have been described by Niggli (*loc. cit.*) and by Hautefeuille and Margottet (*Compt. rend.*, 1881, **93**, 686).

A hydrated lithium metagermanate is formed on mixing fairly strong solutions of sodium metagermanate and a lithium salt. In the cold, it forms a gelatinous precipitate, but on boiling this becomes granular and increases in bulk. The substance was analysed after being washed and dried to constant weight over sulphuric acid (Found: Li_2O, 21·3; GeO_2, 74·4; H_2O, 4·3. $Li_2GeO_3,\frac{1}{3}H_2O$ requires Li_2O, 21·35; GeO_2, 74·4; H_2O, 4·3%).

Hydrated lithium metagermanate is a white, floury substance which does not lose weight when kept over phosphoric oxide for a week. In the air, it slowly absorbs carbon dioxide. Its solubility in water at 25° is 0·85 g. of the anhydrous salt per 100 g. of water. The aqueous solution is strongly alkaline and may be titrated with standard acid. It is readily soluble in dilute mineral acids.

Barium Germanate.—When aqueous solutions of sodium metagermanate and barium chloride are mixed, a pure white, granular precipitate is formed; its composition is variable, however, being dependent on the concentration of the solutions and on the time of washing. One specimen gave: BaO, 35·3; GeO_2, 43·5; H_2O, 21·1%; this analysis corresponds to a very complex formula, the molecular ratios being approximately 3 : 5 : 15. With prolonged washing, the barium content decreased, thus suggesting that the normal germanate, $BaGeO_3$, is hydrolysed progressively. A similar behaviour in regard to barium silicate is described by Le Chatelier in his classical work on the constitution of hydraulic mortars. When the precipitation was carried out in the presence of an excess of baryta or caustic soda, trihydrated barium metagermanate was formed; it was washed rapidly in a Gooch crucible with water, alcohol, and ether (Found: BaO, 48·5; GeO_2, 34·0; H_2O, 17·5. $BaGeO_3,3H_2O$ requires BaO, 49·2; GeO_2, 33·5; H_2O, 17·3%). The discrepancy is due to slight hydrolysis during washing. Barium

metagermanate is a white powder which is slowly decomposed by water. It is insoluble in alcohol and in ether, but readily soluble in dilute acids.

Lead Germanate.—When solutions of sodium metagermanate and lead acetate were mixed, lead metagermanate was formed as a bulky, white, gelatinous precipitate which became granular on heating. It was washed and dried in the air or over calcium chloride (Found: PbO, 65·7; GeO_2, 30·8; H_2O, 3·5. $3PbGeO_3,2H_2O$ requires PbO, 65·7; GeO_2, 30·8; H_2O, 3·5%). It is a white powder practically insoluble in water and insoluble in alcohol and ether, but soluble in dilute mineral acids. At a red heat, it melts to a red, oily liquid and on cooling again it solidifies to a pale yellow solid. It does not decompose on fusion.

Silver Germanate.—Anhydrous silver metagermanate is precipitated when solutions of silver nitrate and sodium metagermanate are mixed (Found: Ag, 64·15; GeO_2, 31·1. Ag_2GeO_3 requires Ag, 64·2; GeO_2, 31·05%). It is a light brown powder which is practically insoluble in water but soluble in acids. It is sensitive to light, being rapidly turned almost jet black in sunlight. On heating, it darkens, melts to a dark liquid, and decomposes with evolution of oxygen. The loss in weight at a red heat is 4·7%. The residue consists of metallic silver and germanium dioxide. Silver germanate is completely soluble in aqueous ammonia.

Summary.

(1) Observations have been made of the rate of displacement of carbon dioxide from the carbonates of lithium, sodium, and potassium by germanium dioxide. The extent and rate of displacement are parallel with the extent to which the various carbonates lose carbon dioxide by dissociation.

(2) Heptahydrated sodium metagermanate has been crystallised from solution. Potassium germanate is too soluble to be crystallised.

(3) Metagermanates of lithium, barium, lead, and silver have been prepared by precipitation with sodium metagermanate.

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CCCLXXVIII.—*The Preparation and Hydrolysis of the Isomeric Azoxybenzyl Bromides.*

By JOHN BALDWIN SHOESMITH and WILLIAM EDMUND TAYLOR.

As a result of recent work on the hydrolysis of substituted benzyl halides by aqueous alcohol it may be stated that, in a series of isomeric benzyl halides, those isomerides in which the $-CH_2Hal$

group is attached to the carbon atom of the benzene nucleus which is attacked during substitution of the corresponding benzene derivative are the ones from which the halogen is most readily removed by the hydrolysing agent named (compare Olivier, *Rec. trav. chim.*, 1923, **42**, 775). This rule holds for the relatively simple OMe, CH_3, F, Cl, Br, I, NO_2, and CO_2H derivatives; ω-bromo-*o*-toluic acid, however, is an exception because of steric influences (see Olivier, *loc. cit.*; Lapworth and Shoesmith, J., 1922, **121**, 1391; Shoesmith and Slater, this vol., p. 214).

It has now been found that the rule also holds for the more complicated azoxybenzyl bromides of the general formula $CH_2Br{\cdot}C_6H_4{\cdot}\overset{\frown}{N{\cdot}O{\cdot}N}{\cdot}C_6H_4{\cdot}CH_2Br$. Azoxybenzene, on treatment with nitric acid, gives the *o*- and *p*-nitro-derivatives (Zinin, *Annalen*, 1860, **114**, 218), and therefore, according to the above rule, the rates of hydrolysis of the bromides should be *o* and $p>m$. This is so, for the rates in aqueous propyl-alcoholic solution are in the order $o>p>m$. This, incidentally, is the first case in which the ortho-compound is the most readily hydrolysable isomeride.

Experimental.

o-Azoxybenzyl Bromide.—*o*-Nitrobenzyl alcohol (Shoesmith and Hetherington, J., 1924, **125**, 1316) in aqueous-alcoholic solution was reduced with zinc dust to the hydroxylamine (Bamberger, *Ber.*, 1903, **36**, 837), which, without being isolated, was oxidised to *o*-azoxybenzyl alcohol (needles, m. p. 123°, from benzene) by hydrogen peroxide or air. The azoxy-alcohol was dissolved in hot benzene, and dry hydrogen bromide passed through the solution; the syrup that separated crystallised when kept under alcohol and was the hydrobromide of an unknown, complex base. When the solution was saturated (three passages of hydrogen bromide were essential), the benzene was almost completely removed *under diminished pressure* on the water-bath. Towards the end of the operation, the temperature was not allowed to rise above that of the room, otherwise violent decomposition of the bromide always took place. The residue crystallised from a small quantity of alcohol in colourless, long plates of *o-azoxybenzyl bromide*, m. p. 105° (violent decomp. at 106°) (Found: hydrolysable Br, 41·3. $C_{14}H_{12}ON_2Br_2$ requires Br, 41·7%).

m-Azoxybenzyl Bromide.—*m*-Nitrobenzyl alcohol, prepared from *m*-nitrobenzaldehyde, was converted into *m*-azoxybenzyl alcohol, m. p. 86° (Carré, *Compt. rend.*, 1905, **141**, 595), in the above manner and further into the corresponding azoxybenzyl bromide in hot benzene solution by means of dry hydrogen bromide, the operation

proceeding quite smoothly with separation of a small quantity of resin. m-*Azoxybenzyl bromide* crystallises from alcohol in pale yellow plates, m. p. 119° (Found: hydrolysable Br, 41·3%).

p-*Azoxybenzyl Bromide.*—*p*-Nitrobenzyl alcohol (m. p. 92°) was converted by the above method into p-*azoxybenzyl alcohol*, which crystallised from benzene (or much water) in pale yellow needles, m. p. 167° (Found: N, 10·7. $C_{14}H_{14}O_3N_2$ requires N, 10·9%). A mixture of the azoxy-alcohol (2 g.) and phosphorus pentabromide (6 g.) in bromoform (20 c.c.) was heated for 3 hours on the water-bath, and the bromoform (10 c.c.) then distilled off. The crude p-*azoxybenzyl bromide* which separated from the residue crystallised from acetone in pale yellow needles, m. p. 203° (Found: Br, 42·0%).

Hydrolysis of the Isomeric Azoxybenzyl Bromides.—Owing to the slight solubility of the *p*-isomeride in ethyl alcohol, the hydrolyses were carried out in aqueous propyl alcohol. Approximately 0·05 g. of the bromide was rapidly dissolved in 20 c.c. of propyl alcohol on the water-bath, 2 c.c. of water were added, and the whole was placed in the vapour of carbon tetrachloride for a definite time. In the table, w is the weight in grams of the bromide, t the time in hours from the addition of the alcohol, and x the percentage of the bromide changed, estimated by titration of the liberated hydrobromic acid with $N/20$-ammonia.

	o-Isomeride.		*m*-Isomeride.		*p*-Isomeride.	
t.	*w*.	*x*.	*w*.	*x*.	*w*.	*x*.
0·6	0·0496	60	—	—	—	—
1	0·0483	97	0·0530	22	0·0500	32
2	0·0564	100	0·0535	40	0·0470	53
4	—	—	0·0544	63	0·0500	77
8	—	—	0·0522	88	0·0506	96

A slight colour change was noticeable in the *o*-isomeride, but not in the other two.

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EDINBURGH UNIVERSITY. [*Received, July 30th*, 1926.]

CCCLXXIX.—*The Photochemical Decomposition of Aqueous Oxalic Acid Solutions.*

By ARTHUR JOHN ALLMAND and LEWIS REEVE.

A CERTAIN amount of work has already been done on the photolysis of oxalic acid. The decomposition of the solid was first noted by Berthelot and Gaudechon (*Compt. rend.*, 1911, **152**, 262), using the

full light of a quartz–mercury lamp placed a few cm. from the oxalic acid contained in a quartz tube over mercury. The production of carbon dioxide and of formic acid is the first result, the latter substance undergoing further decomposition with liberation of more carbon dioxide, and of carbon monoxide, hydrogen, and methane (*ibid.*, 1910, **151**, 478). In a subsequent paper (*ibid.*, 1914, **158**, 1791) they reported that sunlight, acting for 3 months on the solid acid (in quartz), had no visible action, and concluded that wave-lengths shorter than 300 μμ were necessary for the decomposition. Further experiments with the quartz lamp confirmed their first results—the products were formic acid and a gaseous mixture of composition CO_2, 87; CO, 9·5; H_2, 3·5%. The reaction has also been investigated by Noyes and Kouperman (*J. Amer. Chem. Soc.*, 1923, **45**, 1398), more particularly from the point of view of the kinetics of the reaction and of the effect of wave-length. They found that the shorter the latter the more rapid the reaction. Wave-lengths longer than 250 μμ were inactive. Large induction periods were noticed, and water was shown to be a positive catalyst. The hydrated acid decomposed far more rapidly than the anhydrous substance.

Berthelot and Gaudechon (*Compt. rend.*, 1914, **158**, 1791) were also the first to work on the photolysis of the aqueous solution. Just as with the solid acid, continued exposure to sunlight was without effect. Insolation by the quartz–mercury lamp with interposition of a glass screen 0·14 mm. thick (cutting off rays below 250 μμ) caused slow decomposition of an 8% solution, with production of formic acid and a gaseous mixture of composition CO_2, 88—90; CO, 10—12%. The quantity of gas collected never exceeded 1 c.c. When experiments were carried out in the absence of the glass screen, the results were different. After 90 minutes' exposure, formic acid could be detected in the solution, and the composition of the gases was CO_2, 62; CO, 10; H_2, 28%; but after 16 hours' exposure neither formic acid nor carbon monoxide was present, the gases consisting of CO_2, 67; H_2, 33% (greater in volume than after the shorter exposure, but by no means increased in proportion to the longer time). Further prolonged insolation merely resulted in increasing the quantity of gas produced, but left its composition unchanged. Traces of formaldehyde were at the same time found in the liquid. The production of formaldehyde and, in addition, of reducing sugars was also noticed in this photolysis by Baly, Heilbron, and Barker (J., 1921, **119**, 1025) as a result of 40 hours' insolation of a saturated solution by a quartz–mercury lamp.

The conclusions of Berthelot and Gaudechon were, briefly,

(*a*) that the fundamental reaction in the photo-decomposition of aqueous oxalic acid sets in below 300 μμ and is $H_2C_2O_4 \longrightarrow CO_2 + H{\cdot}CO_2H$; (*b*) that, in the wave-length region 300—250 μμ (middle ultra-violet), the formic acid produced undergoes a secondary decomposition $H{\cdot}CO_2H \longrightarrow H_2O + CO$; and (*c*) that, below 250 μμ (extreme ultra-violet), the secondary decomposition $H{\cdot}CO_2H \longrightarrow CO_2 + H_2$ takes place, and, moreover, completely—so that in light of this spectral region oxalic acid is decomposed according to the total equation $H_2C_2O_4 \longrightarrow H_2 + 2CO_2$. No explanation is given as to what happens during long exposures in the complete light of the lamp to the carbon monoxide which is formed during the first few hours and which they consider to be the result of the photo-decomposition of formic acid by light of wave-length 250—300 μμ. Light of this wave-length, it may be remarked, was present throughout the 16-hour run referred to above, during which the previously-formed carbon monoxide disappeared.

Our experiments were commenced with the two purposes of investigating the reaction quantitatively from the point of view of energetics and of examining the mechanism proposed by Berthelot and Gaudechon with a view to clearing up certain discrepancies, of which that quoted above is the most striking. The work proved difficult, and more than 2 years were required to get definitive results. Since it was finished (in May 1923), papers dealing with the subject have been published by Volmar (*Compt. rend.*, 1925, **180**, 1172; see also *ibid.*, 1924, **178**, 697) and by Anderson and Robinson (*J. Amer. Chem. Soc.*, 1925, **47**, 718). Volmar attempted to calculate the threshold frequency necessary for the photolysis of oxalic acid solutions by equating the heat of decomposition of a molecule of the acid to the size of the quantum which would just suffice to break it up. He obtained wave-lengths of 320 μμ for decomposition according to the equation $H_2C_2O_4 \longrightarrow CO_2 + H{\cdot}CO_2H$, and 210 μμ for the secondary reaction $H{\cdot}CO_2H \longrightarrow CO_2 + H_2$. Hydrogen should therefore only be a product of oxalic acid photolysis when working with very short wave-lengths, and this agreed with the results of Berthelot and Gaudechon. Volmar did not attempt to deal with the reported formation of carbon monoxide. Anderson and Robinson insolated a 0·1*N*-solution with the total light of a quartz–mercury lamp, following the reaction by titration with potassium permanganate solution, and measuring the absorbed light by a thermopile–galvanometer combination. Assuming the average size of the absorbed quanta to be 7×10^{-12} erg (corresponding to a wave-length of about 283 μμ), they calculated an average quantum efficiency of 1/1392 for the whole spectral region.

Preliminary Experiments.

It was recognised at the commencement of the work that following the reaction by titration methods would be unlikely to give accurate results. The decomposition is slow, and the products of reaction formic acid and perhaps formaldehyde, are difficult of estimation in the presence of a large excess of oxalic acid. In any case, the nature and the proportions of the gaseous products were matters of primary interest, and it was decided at the outset to concentrate on their investigation and estimation. It soon became evident that there was no possibility of quantitative results when working at atmospheric pressure, owing to gaseous supersaturation. It was also established that the rate of evolution of gas was of the order of 0·1 c.c. per hour with the cell then in use in the full light of a quartz–mercury lamp (iron and carbon arcs were even less effective). It was therefore clear (*a*) that the gases would have to be removed by evacuating the insolated solution, and (*b*) that some form of micro-gas technique would have to be employed for their measurement and analysis.

Apparatus 1, in which insolation cell and capillary measuring tube were fused together, and apparatus 2, in which the evolved gases were swept out through greased taps by mercury, both failed, owing, respectively, to the impossibility of adequate preliminary evacuation and to the gas becoming trapped by greasy mercury. These difficulties were surmounted as follows. The two photochemical cells employed were circular in cross-section, of glass, and with plane ends of polished quartz cemented on. Both were 5 cm. deep, their respective internal diameters being 5 and 7·5 cm., and their volumes 98 and 221 c.c. When in use, connexion was made by means of a side-tube and a mercury-sealed ground joint with a mercury-sealed three-way tap, and then, through a phosphorus pentoxide tube, with a Toepler pump. The larger cell had, cemented on its front, a 1 cm. quartz–water cell to absorb the heat rays. The Toepler pump was of the ordinary pattern, except that the usual ground-glass, mercury-tight valve was absent. In its place, the side-tube connecting with the photochemical cell was continued vertically upwards for such a distance that, when discharging the gaseous contents of the barrel into the gas-delivery pipette, no mercury could pass back into the apparatus. The purpose of this change was to avoid possible trapping of bubbles at the ground-glass surfaces. The gases were collected and transferred by means of the usual technique (see Travers, "Study of Gases"). With this apparatus (apparatus 3), working in the way presently to be described, results satisfactory within limits were obtained, casual losses of gas being practically eliminated.

The measurement and analysis of the gases were carried out by methods which have already been described (Reeve, J., 1924, **125**, 1946). It need only be mentioned here that the technique finally developed allowed of measurements of volume with an absolute accuracy of about 0·0002 c.c., the volume of a single division in the capillary measuring tube employed being 0·000547 c.c. As will be seen, the samples of gas dealt with in the course of the work differed very much in volume, but were generally of the order of 100 divisions, *i.e.*, 0·05 c.c. When fully developed, the analytical methods used for carbon dioxide (absorption by solidified fused potassium hydroxide), hydrogen, and carbon monoxide (explosion with oxygen at ordinary or reduced pressure) enabled us, we estimate, to determine the quantities of these gases present to about the same absolute accuracy as in the total volume measurement. At the stage of the work now being described, however, the methods of dealing with very small amounts of hydrogen and carbon monoxide had not been worked out.

Results with Apparatus 3.

Experiment 1. The smaller cell (98 c.c. capacity) was charged with 90 c.c. of 0·097*M*-oxalic acid and the apparatus evacuated by the Toepler pump, the tap connecting the cell with the pump being occasionally opened for a short interval and then closed. The final traces of air were difficult to remove, and *two weeks* of pumping were found necessary for the purpose. The amount of water lost by evaporation only affected the concentration to a fraction of 1%. Insolation was then started, using the full light of a 110-volt quartz–mercury lamp, placed at the focus of a quartz condenser lens, and with a quartz–water cell stationed between the lens and the photochemical cell in order to cut out the heat rays. After 5 hours' insolation, the lamp was switched off, and the gases produced (almost entirely still dissolved in the solution) were pumped off. It was found impossible in practice to remove them completely, the last traces being held with great tenacity. Instead of this, the cell was opened to the pump and shut off again for a definite number of times (usually four), cell and pump remaining in connexion with one another for 15 seconds on each occasion. Another 5 hours' insolation was given, and the same procedure repeated. After the first few treatments of this kind, it was found that the same amount of gas, of the same composition, was pumped off after each insolation. We concluded that, in consequence of our uniform procedure, the same conditions with regard to gas saturation were being reproduced after each quadruple evacuation, and, therefore, that the gases collected in this manner actually

represented the decomposition brought about by the light during the previous exposure.

The results obtained after conditions had become constant are given below (volumes expressed as divisions, *i.e.*, 0·000547 c.c.). The time of insolation was 5 hours in each case.

Total vol. of gas.	Vol. of CO_2.	Vol. of CO.	Residue.
146	130	5·5	10·5
150	133·5	5	11·5
147	130	7·5	9·5
150	137	—	—

Considering the nature of the work, the degree of reproducibility must be considered good. Although the residual gas samples, after absorption of the carbon dioxide, were exploded with oxygen, the technique of working with these small quantities had not been fully developed, and consequently no figure can be quoted for the quantity of hydrogen present. The amount of carbon monoxide could, however, be calculated from the diminution in volume observed on treatment with potash after the explosion. The greater part of the residue (col. 4) was probably air (leakage during the experiment or unremoved during the preliminary evacuation).

Experiment 2. The larger cell (221 c.c. capacity) was used, filled with 0·5*M*-oxalic acid, and another lamp employed, of rather different energy distribution. The preliminary evacuation took well over *three weeks*. In order to get an idea of the proportion of hydrogen present in the gas, the residues (after carbon-dioxide absorption) from a number of the separate insolations were collected together, and the whole was analysed for carbon monoxide and hydrogen. Below are given results of *all* the separate 3-hour insolations, including those made before constant conditions had been reached (volumes of gas in " divisions " as before).

Total vol. of gas	—	217	228	234	247	266	252	249
Vol. of CO_2	189	195	207·5	—	226	247	238	235

The vols. of CO and H_2 were 8 and 3·5 respectively (average of collected samples).

It will be seen that, again, after the first few insolations, the volume of gas (and its percentage of carbon dioxide) produced by a 3-hour exposure became practically constant, the experimental error being of the order of 5%. This error is due rather to imperfections in the method of collection or to inconstancy in the light source than to errors in measurement or analysis, which are certainly less than 1%. The small residue unaccounted for apparently decreased during the course of the experiment, and probably was due to air unremoved at the start.

These two experiments demonstrated that, under constant

conditions (the concentration of the oxalic acid of course hardly altered during an experiment), the rate of decomposition was constant—a result to be anticipated, but nevertheless valuable as showing to what extent the experimental technique could be relied on. They also, however, made clear the necessity of modifying the latter in such a way as to eliminate the weeks of preliminary evacuation, and so permit of more rapid working. As experience had shown that the larger the volume of solution the longer the time required for evacuation, it was obviously desirable to reduce the size of the cell as much as possible. Consequently, a cell of similar construction to those hitherto used, but of only 2·5 cm. internal diameter, was made up; its volume was about 24·5 c.c. Further, in order to increase the uniformity of the so-called " parallel " beam of light employed, and so make it possible to determine its total energy flux more exactly, the mercury lamp was fitted with a diaphragm provided with a circular aperture (several were used on different occasions, their diameters being 1·0, 1·4, and 1·8 cm.; most measurements were done with 1·4 cm.). At the same time, in order to increase the intensity of the incident light, and thus bring about a total decomposition of about the same order as before, the parallel beam was passed through a second quartz condenser, thereby being turned into a convergent beam directed on to the front of the cell, and brought to a focus about half-way through the oxalic acid solution. These changes (the whole as modified constituting apparatus 4) were successful. The time required for complete preliminary evacuation was reduced to 2—3 days (the increase in concentration owing to loss of water was about 0·25%), and, moreover, it was found possible to pump off completely the gaseous products of photolysis after exposure, and thus to eliminate one uncertain source of error. Naturally, in order to get reproducible results during the insolation, very great care had to be taken to have cell, lenses, and lamp in precisely the same relative positions during every exposure.

Results with Apparatus 4.

It was first of all necessary to test the proportionality between extent of reaction and time of exposure with the new experimental arrangement. This was done as follows.

Experiment 3. A solution of oxalic acid was exposed for 23·75 hours. The gaseous products (in divisions) were: CO_2, 297; CO, 7; H_2, undetermined. It was then re-exposed for 7 hours, and there were produced: CO_2, 95; CO, 2; H_2, 1. Assuming a constant rate of reaction, the 7-hour exposure should have given: CO_2, 87·6; CO, 2. As it was thought that a slight shift in the

apparatus had taken place between the two exposures, thus causing the discrepancy in the carbon dioxide value, the experiment was repeated.

Experiment 4.

	Found for 17·7 hrs.	Calc. for 7·5 hrs.	Found for 7·5 hrs.
CO_2	226·5	96	94
CO	4·0	1·7	1·8
H_2	4·4	1·9	1·8

The agreement is satisfactory.*

We then directed our attention to the effect of wave-length.

Experiment 5. A 0·68*M*-solution of oxalic acid was insolated for a considerable period by a beam which had passed through a filter consisting of 5 mm. of a 0·2% aqueous quinine sulphate solution, and was therefore free from ultra-violet light. No perceptible decomposition resulted. This was to be expected, as oxalic acid shows no absorption in the visible region. It is nevertheless evidence that the material used was free from traces of such impurities as iron, which are known to sensitise its photolysis in visible light. It may be mentioned that 10 g. of the acid, on incineration, left no visible residue.

Experiment 6. According to Berthelot and Gaudechon, oxalic acid solutions are not affected by light of wave-length longer than 300 μμ. As, however, their technique was clearly not capable of detecting such small amounts of decomposition as ours, and as our measurements (quoted later) had shown oxalic acid solutions to absorb appreciably at 365 μμ, we insolated the same 0·68*M*-solution in quartz–mercury light which had passed a filter consisting of 5 mm. of 0·075% solution of Casella's Diamond Fuchsin (large crystals), held between quartz plates. This cell replaced the water cell used in Expts. 1—4. The solution has been shown in this laboratory to pass 30% of the incident 365 μμ radiation, about 1·2% of both the 313 μμ and the 405 μμ lines, and otherwise nothing except in the red. The result of 25 hours' insolation was the production of 4·5 divisions of gas, all carbon dioxide within the limits of accuracy of our technique. Carbon monoxide and hydrogen, if present in the same proportions as in previous insolations, would have been undetectable. This quantity of gas, although small, undoubtedly represents a real decomposition, and we therefore conclude that oxalic acid solutions are photosensitive to light of wave-length 365 μμ. (This and the next few experiments were

* When determining carbon monoxide and hydrogen in the gaseous residue left after absorbing carbon dioxide, the residue in this and in subsequent experiments was given a preliminary sparking *before* adding oxygen. This point is of importance and will be discussed later.

carried out under conditions which enabled the subsequent calculation of quantum efficiencies.)

The next point of interest was to determine whether the proportions of hydrogen and carbon monoxide in the products of decomposition altered with wave-length. According to Berthelot and Gaudechon, this is the case, carbon monoxide being a secondary product of decomposition between 300 and 250 μμ, and hydrogen below 250 μμ.

Experiment 7. A 0·62*M*-solution was exposed for 28 hours behind a filter (in quartz) of 5 mm. of 0·0125% Auramin O (no water cell employed). Measurements in this laboratory have shown that such a solution transmits thus:

254 μμ	Nil.	297 μμ	0·40
265	Possible trace.	303	0·368
280	0·251	313	0·263
290	0·364	365	Nil.

The volumes of gas obtained were CO_2, 73·5 divs.; CO and H_2, each 1·5 div. An exposure to the full light of the lamp at that time gave, per 73·5 divs. of CO_2, 1·3 divs. CO and 1·4 divs. H_2, *i.e.*, the same proportions within experimental error.

Experiment 8. A 0·62*M*-solution was then exposed for 22·8 hrs. behind a filter consisting of 1 cm. of chlorine at atmospheric pressure between quartz plates. The quartz–water cell was used in addition. The transmission of the complete filter in the ultra-violet region (more accurate data have since been obtained) was determined approximately as:

248 μμ	0·50	270 μμ	0·50	290 μμ	0·15	313 μμ	0·035
254	0·50	275	0·45	297	0·12	334	0·085
265	0·50	280	0·40	303	0·11	365	0·13

It may be mentioned that a cement containing pitch had been used for attaching the quartz plates to the hollow glass block employed in the construction of this filter. Although chlorine gas was passed through for 2 days before sealing the filter off, and the transmission remained apparently unchanged over a period of 2 months, it is probable that vapours of some chlorinated material present were the cause of the discrepancies found between the observed transmissions and those of a pure chlorine filter.

The resultant gases were CO_2, 70 divs.; CO, 5 divs.; H_2, 4 divs. Under the same conditions with the total light of the lamp, about 1·3 divs. of each of carbon monoxide and hydrogen would have been obtained per 70 divs. of carbon dioxide. The effect of decreasing the average incident wave-length is thus to increase very considerably the proportion of gases other than carbon dioxide resulting from the photolysis. When the impure nature of the light passed

by the chlorine filter is taken into account, the relative increase is even greater than appears from the above data. On the other hand, there is no sign of any variation in the proportions of carbon monoxide and hydrogen with change in frequency, as was found by Berthelot and Gaudechon.

Mechanism of the Reaction.

In discussing these results, it must be remembered that they hold for the *initial* stages in the photolysis of oxalic acid solutions —in no case was more than a very small fraction of the acid decomposed. It was therefore not likely that the carbon monoxide and hydrogen arose by secondary photo-decomposition of the traces of primarily-produced formic acid, and this view was confirmed by later work on the quantum efficiency of formic acid decomposition (see following paper) combined with a knowledge of the extinction coefficients of the two acids. In any case, however, the production *both* of carbon dioxide *and* of the other gases has been shown to proceed at a constant rate, independent of the extent of decomposition (which was in its initial stages). But if carbon monoxide and hydrogen resulted from a secondary photo-decomposition, then the amounts produced should clearly be proportional to the *square* of the time, in consequence of the continually increasing formic acid concentration.

A possible explanation is that definite fractions of the oxalic acid molecules decompose directly on absorption of light according to the equations

$$(a)\ H_2C_2O_4 \longrightarrow 2CO_2 + H_2,$$
$$(b)\ H_2C_2O_4 \longrightarrow CO_2 + CO + H_2O,$$

or, which amounts to practically the same thing, that definite fractions of the primarily-produced formic acid molecules have particularly high energy contents at their instant of formation, and decompose further in accordance with the equations

$$(a)\ H{\cdot}CO_2H' \longrightarrow H_2 + CO_2,$$
$$(b)\ H{\cdot}CO_2H' \longrightarrow H_2O + CO.$$

Such assumptions would explain the constant rate of production of hydrogen and carbon monoxide, but, in order to account for the relative proportions in which they appear, it would be necessary to assume further that the probabilities of the reactions (*a*) and (*b*) are of the same order.

Another possibility, however, suggested itself. It is well known that formaldehyde results in many cases when organic substances are exposed to ultra-violet light, including sunlight (*e.g.*, Moore and Webster, *Proc. Roy. Soc.*, 1918, *B*, **90**, 168; Baly, Heilbron, and

Barker, *loc. cit.*; Dhar and Sanyal, *J. Physical Chem.*, 1925, **29**, 926). In particular, the production of formaldehyde in this reaction had been reported by Berthelot. One could imagine it to be formed by interaction between nascent or " activated " carbon dioxide molecules of high energy content and water, in accordance with the equation $CO_2' + H_2O \longrightarrow H{\cdot}CHO + O_2$, as was suggested by Baly, Heilbron, and Barker (who also remarked its occurrence as a product of the present reaction). If it were actually present, but undetected, it would behave when subjected to analysis by our methods as a mixture of carbon monoxide and hydrogen—and, moreover, 1 vol. of formaldehyde vapour would behave like a mixture of 1 vol. of carbon monoxide plus $\frac{1}{3}$ vol. of hydrogen. For, on explosion with oxygen, we should have, in the one case

$$\text{Residue} + \underbrace{H{\cdot}CHO + O_2}_{2\text{ vols.}} \longrightarrow \underset{1\text{ vol.}}{H_2O + CO_2} + \text{Residue},$$

and, in the other,

$$\text{Residue} + \underbrace{CO + \tfrac{1}{3}H_2 + \tfrac{2}{3}O_2}_{2\text{ vols.}} \longrightarrow \underset{1\text{ vol.}}{\tfrac{1}{3}H_2O + CO_2} + \text{Residue},$$

i.e., in either event, the contraction, both after explosion and also after subsequent treatment with potash, would be 1 vol. If, on the other hand, a gaseous mixture, free from hydrogen and carbon monoxide but containing formaldehyde, were sparked beforehand, there should be an increase in volume corresponding to the equation $H{\cdot}CHO \longrightarrow H_2 + CO$, and, on subsequent combustion with oxygen, the ratio $H_2 : CO$ found should be 1 : 1, and the absolute volume of either gas would be equal to the volume of formaldehyde present in the original mixture.

After the possibility of accounting in this way for the apparent hydrogen and carbon monoxide contents of the products of photolysis had occurred to us, the gaseous residues, after removal of carbon dioxide, were sparked before adding oxygen and exploding. The result was *always* an increase in volume, equal, within experimental error, to the absolute amounts of *either* hydrogen *or* carbon monoxide found during the subsequent analysis. The residues from Expts. 4, 7, and 8 were treated in this way, with the following results (volumes in divisions):

Expt. No.	Increase in vol. on sparking.	Vol. of CO.	Vol. of H_2.
4	4·0	4·0	4·4
7	1·5	1·5	1·5
8	5	5	4

On the other hand, in those experiments (2 and 3) in which the explosion with oxygen was carried out without a preliminary sparking of the gas, the ratios CO : H_2 found were 2·3 : 1 and 2 : 1, respectively. When the minute quantities of gas dealt with are remembered, the discrepancy between these figures and the ratio 3 : 1 is not surprising.

To confirm the probable conclusion that what we had originally taken for a mixture of carbon monoxide and hydrogen was really formaldehyde, this substance was tested for in solutions of oxalic acid which had been exposed to light, but not subsequently evacuated. None was found when using apparatus 4, even after a 26-hour exposure of a 0·7*M*-solution. Nor was a positive result anticipated, assuming that the total amount formed corresponded to the quantity pumped off and detected by our method of gas analysis, as it would lie outside the limits of sensitivity of the Buchanan–Schryver test employed. When, however, an identical solution was exposed in a quartz test-tube to the full light of the quartz–mercury lamp at a distance of 7 cm., a distinct positive test was obtained.

One further point may be mentioned. We have suggested a mechanism of formaldehyde formation which involves the simultaneous production of oxygen, molecule for molecule; and it might be asked why, this being the case, when the residues were given their preliminary sparking, the reaction $H{\cdot}CHO + O_2 \longrightarrow H_2O + CO_2$ did not take place. In this connexion, it must be remembered (1) that the photolysis products, after removal of carbon dioxide, contained an excess of residual gas, probably air, (2) that the sparking was carried out at reduced pressure (Reeve, *loc. cit.*, pp. 1951, 1952), and (3) that the sparking bulb had a maximum diameter of only 2—3 mm. All these factors would tend to limit the explosion range, and, taken together, are enough to account for inhibition of the explosion. The *dissociation* of formaldehyde on sparking would not be affected in the same way. It is a unimolecular reaction, and, if regarded as a purely thermal one, is known to take place at a low temperature. Of course, other mechanisms of formaldehyde formation are conceivable. Thus, a small fraction of the oxalic acid molecules might decompose in accordance with the equation $H_2C_2O_4 \longrightarrow 2CO_2 + H_2'$, the activated hydrogen then reacting further as follows: $H_2' + H_2C_2O_4 \longrightarrow CO_2 + H_2O + H{\cdot}CHO$. We consider an analogous mechanism in the succeeding paper, and the suggestion is one which could be tested in an obvious manner. The fact that, using a *saturated* oxalic acid solution, Baly, Heilbron, and Barker noted the formation, not only of formaldehyde, but also of reducing sugars, is

perhaps significant. On the whole, however, whilst recognising this possibility, we prefer the first mechanism proposed. It is simpler, and has the advantage of accounting for the production of formaldehyde during other organic photolyses.

Our conclusions regarding the mechanism of this photo-decomposition are seen to differ considerably from those arrived at by Berthelot and Gaudechon, who, however, carried the degree of decomposition of their oxalic acid solutions much farther than we did. As it was possible that the increasing accumulation of formic acid in these circumstances might affect the reaction, we took up the subject of the photolysis of this acid, and our results are contained in the next paper.

Energetics of the Reaction.

Expt. 6 and later ones were carried out using beams of light of measured total intensity and spectral energy distribution, thereby making possible the calculation of quantum efficiencies (see, however, later). The total visible and ultra-violet energy in the beam was determined after it had passed the first quartz condenser lens and a 2 cm. quartz–water filter, but before it had been concentrated on to the cell by the second quartz condenser. This was done by means of a Coblentz thermopile and a Broca galvanometer. The distribution of energy over the area of the beam was by no means uniform, and necessitated the taking of a large number of systematic measurements, and averaging the results. The readings thus obtained were converted into absolute units by measuring the deflexion given by the same thermopile combined with a Paschen galvanometer when irradiated by a standard Hefner lamp at 1 m. distance. The sensitivities of the two galvanometers were carefully measured and their slightly differing resistances taken into account. Two lamps were used, the aperture of the diaphragm covering them being 1·4 cm. in every case. The results found for the average total visible and ultra-violet energy under these conditions were:

Lamp 1. 17·73 *H.K.* or 16750 ergs/cm.^{2}/sec.
Lamp 2. 14·03 *H.K.* or 13240 ergs/cm.^{2}/sec.

To get the total energy entering the cell per second, these figures were multiplied by $41{\cdot}7 \times 0{\cdot}9 \times 0{\cdot}95$, representing, respectively, the effective area of the second (concentrating) lens, and corrections for the reflexion losses at the surface of this lens and at the front surface of the cell. The method of measuring the spectral energy distribution in the beams used has been described elsewhere (Franklin, Maddison, and Reeve, *J. Physical Chem.*, 1925, **29**, 713). The final figures obtained with lamp 1 can be applied with some confidence. In the case of lamp 2, some time elapsed between these

determinations and certain of the experiments, thus introducing an uncertain error, which we estimate as being of the order of 10%.

Fresh measurements were made of the extinction coefficients of oxalic acid solutions, using a quartz spectrometer, Coblentz thermopile and Paschen galvanometer. The results, where k (the molecular extinction coefficient) is given by $(1/cd) \log_{10} I_0/I$ (c in g.-mols. per litre, d in cm.), were as follows:

λ.	k.	λ.	k.	λ.	k.	λ.	k.
365 $\mu\mu$	0·0155	303 $\mu\mu$	1·57	280 $\mu\mu$	11·3	265 $\mu\mu$	36
334	0·11	297	2·2	275	21	254	54
313	0·19	290	4·8	270	26	248	58

Bielecki and Henri (*Compt. rend.*, 1912, **155**, 456) give the following values:

λ in $\mu\mu$	300	290	269·3	266·5	255	245·2
k	2·2	4·8	24·6	32	54	61

Beer's law was shown to hold, at least approximately, between concentration limits of 0·5—0·1M for 313 $\mu\mu$ and 0·5—0·01M for 303 $\mu\mu$. For other wave-lengths, the absorption was either too strong or too weak for this law to be tested. The figures for 297 $\mu\mu$ and shorter wave-lengths were obtained with 5 cm. and 5 mm. layers of a 0·01M-solution.

The details of the calculation of quantum efficiency are given for one simple case only.

Quantum Efficiency for 365 $\mu\mu$. This was calculated from the results of Expt. 6, neglecting the very slight absorption of active wave-lengths other than 365 $\mu\mu$. The data were:

Lamp used	No. 1.	k	0·0155.
Duration of expt.	25 × 3600 secs.	Depth of cell	5 cm.
Conc. of oxalic acid ...	0·68M.	Fraction of 365 $\mu\mu$ absorbed	0·114.

Ergs of λ 365 $\mu\mu$ passing water cell $= a = 3270/\text{cm.}^2/\text{sec.}$

Ergs of λ 365 $\mu\mu$ passing filter cell $= b = a \times 0{\cdot}30/\text{cm.}^2/\text{sec.}$

Ergs of λ 365 $\mu\mu$ entering photo-chemical cell $= c = b \times 0{\cdot}9 \times 0{\cdot}95 \times 41{\cdot}7/\text{sec.}$

Ergs of λ 365 $\mu\mu$ absorbed by oxalic acid $= d = c \times 0{\cdot}114/\text{sec.}$

Ergs of λ 365 $\mu\mu$ absorbed by oxalic acid in course of run $= e = d \times 25 \times 3600.$

Quanta of λ 365 $\mu\mu$ absorbed by oxalic acid in course of run $= e \times 10^{13} \div 54.$

$= 6{\cdot}64 \times 10^{19}.$

Carbon dioxide formed $= 4{\cdot}5$ divisions at 15°.

$= 4{\cdot}2$ divisions at *N.T.P.*

$= 4{\cdot}2 \times 0{\cdot}00055$ c.c. at *N.T.P.*

$= 4{\cdot}2 \times 0{\cdot}00055 \times 6{\cdot}1 \times 10^{23} \div 22{,}400$ molecules

$= 6{\cdot}29 \times 10^{16}$ molecules.

Hence quanta absorbed/molecules decomposed $= 1060$ for 365 $\mu\mu$.

Quantum Efficiency for 300 μμ. This was determined from the results of Expt. 7, carried out with lamp 2, and with a filter passing light of wave-lengths 280—313 μμ in proportions already given. The quantities of energy absorbed by the oxalic acid per second for the different components of the radiation were calculated from the spectral energy distribution in the beam, the transmission of the Auramin O filter, and the extinction coefficients of the solution. Absorption was complete up to 303 μμ, and the centre of gravity of the absorbed energy under those conditions lay at about this wave-length. The total number of quanta of mean value 66×10^{-13} ergs absorbed in the 28-hour run was $2{\cdot}625 \times 10^{20}$ and the number of molecules of oxalic acid decomposed, allowance being made for the amount represented by the formaldehyde, was $1{\cdot}07 \times 10^{18}$. Hence, quanta absorbed per molecule decomposed = 245 for 300 μμ.

Quantum Efficiency for 265 μμ. The results of Expt. 8 are utilised for this calculation. As the chlorine filter employed passed large quantities of light elsewhere than between 254 and 275 μμ, of which region 265 μμ was taken as the typical wave-length, the results obtained must be corrected by means of the quantum efficiencies previously determined. (The actual amounts of light absorbed by the oxalic acid for the different spectral regions stood in the ratio 334—365 μμ : 280—313 μμ : 254—275 μμ = 1 : 4·67 : 5·83.) The total number of molecules of oxalic acid decomposed was $10{\cdot}64 \times 10^{17}$. Of these, $0{\cdot}164 \times 10^{17}$ and $2{\cdot}834 \times 10^{17}$ have been calculated as having been decomposed by 365 μμ and the 300 μμ group, respectively. This leaves $7{\cdot}64 \times 10^{17}$ molecules as the share of the 265 μμ group, of which the number of absorbed quanta was calculated as $7{\cdot}65 \times 10^{19}$. Therefore, quanta absorbed per molecule decomposed = 100 for 265 μμ.

It was thought desirable to check these results by means of an experiment done with the whole light of the lamp.

Experiment 9. A 0·68*M*-oxalic acid solution was insolated for 7 hours, merely using a water filter. After correction for loss as formaldehyde and for temperature, the result was the formation of 0·092 c.c. of carbon dioxide at *N.T.P.*, *i.e.*, of $2{\cdot}50 \times 10^{18}$ molecules. The absorbed quanta were calculated as previously, the results being given below, together with the theoretical number of molecules decomposed, assuming the correctness of the above quantum efficiencies:

λ (in μμ).	Ergs absorbed.	Quanta absorbed.	Calc. decomp. (molecules).
248·5—275	$8{\cdot}67 \times 10^{8}$	$1{\cdot}16 \times 10^{20}$	$1{\cdot}16 \times 10^{18}$
280 —313	28·7	4·35	1·78
334 —365	3·86	0·71	0·07

The total calculated decomposition is thus $3{\cdot}01 \times 10^{18}$ molecules,

Considering the nature of the experiments and the uncertain factor with regard to lamp 2 already noted, the agreement with the experimental value of $2{\cdot}50 \times 10^{18}$ is sufficiently good.

We can therefore summarise the efficiency results for a 0·6—0·7*M*-solution as follows :

λ (in $\mu\mu$).	Quanta/molecule.	Quantum efficiency (γ).
265	100	0·01
300	245	0·0041
365	1060	0·00094

The relative values of γ are as generally found—an increase in frequency results in an increased probability of decomposition following on quantum absorption. According to Anderson and Robinson (*loc. cit.*), the average quantum efficiency for the decomposition of a 0·05*M*-oxalic acid solution in the full light of the quartz–mercury lamp is only 1/1392. They estimated the average size of their absorbed quanta as 7×10^{-12} ergs, which corresponds to a wave-length of about 283 $\mu\mu$, for which our results point to a value of γ of about 1/160. We can only conclude, from the fact that these authors were estimating the amount of decomposition by titration with potassium permanganate, that they were under the impression that the decomposition taking place was identical with the most important of the reactions which occur in the presence of uranyl salts, *viz.*, $H_2C_2O_4 \longrightarrow H_2O + CO + CO_2$.

Actually, however, the permanganate titre of their solution would remain constant or diminish very slightly, depending on the exact method of carrying out the titrations, and this would account for the very low quantum efficiency observed.

It may be pointed out that the literature shows how necessary it is to specify the exact reaction which is taking place when discussing oxalic acid photolysis in presence of uranyl and other metallic salts. In addition to the above decomposition, the added salt can oxidise the oxalic acid, being itself reduced, or, if air be present, can act as a carrier for atmospheric oxygen. Whereas Anderson and Robinson find quantum efficiencies much below unity for the uranyl sulphate–oxalic acid mixtures, Boll (*Ann. Physique*, 1914, **2**, 256), working with 0·001*M*-solutions freely exposed to air, obtained a value for γ of 50 for light of nearly the same frequency. In this latter case, the uranyl salt was probably simply acting as an oxygen carrier. The same remark applies, perhaps in a lesser degree, to the photolysis of oxalic acid solutions in absence of a catalyst. For example, in Kailan's work (*Monatsh.*, 1913, **34**, 1209), which, for this reason, we did not quote at the beginning of this paper, the reaction being followed was again probably essentially $H_2C_2O_4 + \frac{1}{2}O_2 \longrightarrow H_2O + 2CO_2$.

Effect of Concentration.

The reaction being apparently unimolecular, we should expect the quantum efficiency to be independent of concentration. We tested this point by experiments with 0·01*M*- and 0·001*M*-solutions, and obtained rather unexpected results.

Experiment 10. A 0·01*M*-oxalic acid solution was exposed to the total light of lamp 2 (1·4 cm. diaphragm aperture) for 15½ hours. The yield of carbon dioxide was 116 divisions at 15°, or 110 divisions at *N.T.P.* This is equivalent to $1{\cdot}65 \times 10^{18}$ molecules. The absorption of the 334 μμ and 365 μμ lines by this dilute solution was negligible. For the other groups of lines, we have calculated as follows:

λ (in μμ).	Ergs absorbed.	Quanta absorbed.	Calc. decomp. (molecules).
280—313	$5{\cdot}18 \times 10^{8}$	$0{\cdot}78 \times 10^{20}$	$0{\cdot}32 \times 10^{18}$
254—275	7·68	1·02	1·02

The observed decomposition thus exceeds the calculated value of $1{\cdot}34 \times 10^{18}$ molecules by nearly one-quarter.

Experiment 11. A 0·001*M*-solution was similarly insolated for 19½ hours. The carbon dioxide yield was 79 divisions, or 75 divisions at *N.T.P.* Calculating as before, and making allowance for the 8% decrease in concentration occurring during the insolation, the volume of carbon dioxide at *N.T.P* expected would be only 40 divisions, or little more than half of what was actually obtained.

It must be remembered that the quantum efficiencies used for obtaining the calculated values are average values for fairly wide spectral regions, and can only be applied for the purposes of exact calculations to cases in which the distribution of absorbed energy over the different wave-lengths comprised within the regions concerned is identical with that which held good during the experiment from which the quantum efficiency was deduced. By plotting our figures for γ against ν and against λ, and by considering the aforesaid energy distributions, we were able to arrive at a rough estimate as to the extent to which our results are affected by this factor. For Expt. 10 we found that the absorbed energy distribution in the 265 μμ group was practically identical with that in Expt. 8, but that the centre of gravity in the 300 μμ group lay roughly at about 284 μμ. The effect would be to increase the expected transformation by about 12%, and thus to halve the apparent discrepancy. In Expt. 11, the average effective absorbed wave-lengths for both spectral regions lie further in the ultra-violet than the conventional figures of 300 and 265 μμ. In the latter case, however, the shift is very small, and the total effect is only to increase the calculated decomposition by about 10%, the actually

observed decomposition still being 70% more than the calculated figure.

We have done no further experiments, and therefore do not wish to lay too much stress on these results. Those of Expt. 11 are, however, certainly far outside our ordinary experimental errors. If they be accepted, it would seem necessary to assume that those oxalic acid molecules which, by absorption of a quantum, are raised to so high an energy level that they can decompose, do not do so instantaneously, but have an appreciable life in the activated condition, during which they are liable to be deactivated by collision with other oxalic acid molecules. An increase in dilution lessens the chance of such deactivation, and hence raises the quantum efficiency. It may be mentioned that, very recently, Ghosh and Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 173) have been led to a similar conclusion in the case of activated bromine molecules undergoing reaction with tartaric acid.

Summary.

(1) The initial stages in the photolysis of aqueous oxalic acid solutions have been quantitatively investigated by specially developed experimental methods.

(2) For wave-lengths between 254 and 365 μμ, the primary reaction is $H_2C_2O_4 \longrightarrow H{\cdot}CO_2H + CO_2$.

(3) Neither hydrogen nor carbon monoxide is produced.

(4) Formaldehyde (the vapour of which is liable to be analysed as a mixture of carbon monoxide and hydrogen) is formed in small quantity, in all probability by interaction between nascent carbon dioxide molecules and water.

(5) The proportion of formaldehyde produced increases with the frequency of the light used.

(6) For solutions of concentration 0·6—0·7*M*, the number of quanta required for decomposition of 1 molecule of oxalic acid are as follows: 265 μμ, 100; 300 μμ, 245; 365 μμ, 1060.

(7) For solutions of concentration 0·01*M* and (particularly) 0·001*M*, there is evidence that the quantum efficiencies are greater than those quoted.

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CCCLXXX.—*The Photochemical Decomposition of Aqueous Formic Acid Solutions.*

By Arthur John Allmand and Lewis Reeve.

A few isolated observations have previously been recorded on the subject of formic acid photolysis. Thiele (*Ber.*, 1907, **40**, 4914; *Z. angew. Chem.*, 1909, **22**, 2472) reports that the anhydrous acid is decomposed by the light from a quartz–mercury lamp. A small quantity of a yellow, hygroscopic, and strongly acid solid is produced, whilst the gaseous products consist chiefly of carbon dioxide, but also contain oxygen, carbon monoxide, and other combustible gases. Berthelot and Gaudechon (*Compt. rend.*, 1910, **151**, 478) give the composition of the gases produced as: CO_2, 59; CO, 21; H_2, 19; CH_4, 1%. The same authors, whilst ascribing an important part in the photolysis of aqueous oxalic acid to secondary photo-decomposition of primarily-produced formic acid, bring forward no experimental work with aqueous formic acid solutions in support of their views. Indeed, the only published work on this subject is that of Kailan (*Z. physikal. Chem.*, 1920, **95**, 215), who merely records (i) that such solutions are decomposed by ultraviolet light when contained in quartz, but not in glass, vessels; (ii) that the dissociation constant of the acid is unchanged after partial photolysis and that, therefore, oxalic acid is not a product; (iii) that the velocity increases with increase of concentration, but less rapidly. Ramsperger and Porter (*J. Amer. Chem. Soc.*, 1926, **48**, 1267) report that formic acid vapour gives, on photo-decomposition, a gaseous mixture containing CO_2, 18; H_2, 18; CO, 32; H_2O, 32%.

Experimental.

Our own experiments, made in order to test Berthelot's suggested mechanism for photo-decomposition of oxalic acid solutions, have not been carried as far as we could have wished, but nevertheless present points of interest. The apparatus used comprised the essential features of Apparatus 4 (preceding paper), but, in addition, included, between the insolation cell and the pump, a trap containing solid potash, its purpose being to retain formic acid given off during the preliminary evacuation. Vacuum taps, suitably placed, made it possible to connect the cell with the Toepler pump (*a*) directly, (*b*) *via* the phosphorus pentoxide tube, and (*c*) *via* the potash trap and the phosphorus pentoxide tube. The preliminary evacuation could be carried out (as described in the preceding paper) efficiently and sufficiently rapidly with the above

arrangement. In order to deal with the products of photolysis, a large expansion bulb was attached to the apparatus between the cell and the absorption tubes, separated from both of them by taps and leading, in its turn, by means of a vacuum tap and ground joint, to a bulb which could be cooled either in liquid air or in a solid carbonic acid–ether mixture.

The procedure adopted after insolation was (i) to evacuate the whole of the apparatus except the cell; (ii) to cool the freezing-out bulb by liquid air; (iii) all other taps being closed, to put the cell into connexion with the expansion bulb for a definite short period; (iv) to shut off the cell from the expansion bulb and connect the latter with the freezing-out bulb; (v) after sufficient time had elapsed, to pump off through the phosphorus pentoxide tube, measure, and analyse any gases which had escaped condensation at liquid-air temperature [fraction (*a*)]; (vi) to replace the liquid air in the Dewar vessel surrounding the freezing-out tube by solid carbon dioxide and ether, and then pump off, measure, and analyse as before [fraction (*b*)]. The residual contents of the freezing tube after (vi) were merely formic acid and water.

Experiment 1. After showing that the preliminary evacuation had no appreciable effect on the concentration of the formic acid solution in the cell, a 2·40*M*-solution was insolated for 18·28 hours in the total light of the quartz–mercury lamp, and the products were separated as described. Fraction (*a*), *i.e.*, gas not condensed by liquid air, measured 0·356 c.c. A portion of it gave a strong positive formaldehyde reaction with the Buchanan–Schryver test. This was surprising, as one would have imagined all formaldehyde to be condensed at liquid air temperature, recent measurements of Mali and Ghosh (*J. Indian Chem. Soc.*, 1924, **1**, 37) pointing to the vapour pressure of Kekulé's liquid formaldehyde as being of the order of 10^{-7} mm. under those conditions. It seems possible that the vapour given off from Kekulé's product does not consist of simple formaldehyde molecules, but of something more complex (no vapour density measurements appear to have been done), and that, on the other hand, unimolecular formaldehyde might be expected to behave like a permanent gas in respect of its condensation temperature. In our experiments, it is formed at room temperature and pumped off at a pressure of about 0·0005 atm. In these circumstances, its tendency to polymerise (so marked at higher temperatures and pressures) would be very much reduced.

When another portion of fraction (*a*) was subjected to sparking in the micro-gas analysis apparatus previously described, it increased considerably in volume, and subsequent analysis showed carbon dioxide to be absent and the sparked gas to consist of carbon

monoxide and hydrogen, with a small residue (air from leakage). The actual results were as follows:

(*a*) Volume of gas taken	.....	62	divisions.
(*b*) " " after sparking	.....	90	"
(*c*) " " " treatment with KOH	.....	91	"
(*d*) " " " addition of oxygen	.....	173	"
(*e*) " " " combustion	.....	90	"
(*f*) " " " treatment with KOH	.....	41	"

Hence

(*g*) CO in sparked gas	.....	49	"
(*h*) H_2 " "	.....	39	"
(*k*) H·CHO in original gas	.....	28	"
(*l*) Composition of original gas: H·CHO	.....	28	"
CO	.....	21	"
H_2	.....	11	"
Residue	.....	2	"

Fraction (*b*)—condensed by liquid air, but not by solid carbon dioxide and ether—had a total volume of 15·91 c.c. On treatment of a micro-portion with solid potash, it proved to be almost entirely carbon dioxide. The whole sample of 15·9 c.c. was then treated with potash in the same way. The total residue amounted to 158 divisions, or 0·0869 c.c. only. We are unable to say exactly what was the composition of this gas. It was not formaldehyde, nor did it give the latter even on long standing with water (Buchanan–Schryver test). On continued sparking, however, in absence of oxygen, its volume increased until it was about eight times that of the original sample—thus a volume originally 21·5 divisions became successively 56, 84, 144, 161, 164·5, 171·5, 172, 171 divisions, and this final figure remained unaltered even after more than 50 sparkings. The sparked gas was then divided into three portions, each of which was analysed for carbon monoxide and hydrogen. The results were:

(i) CO, 42; H_2, 57%. (ii) CO, 40; H_2, 58%. (iii) CO, 43; H_2, 56%.

The gas unaccounted for never amounted to more than one division (0·00055 c.c.) in any single analysis. If the total gas unaccounted for (about 2·5 divs.) be regarded as due to air leak, and subtracted from the 21·5 divs. of the original gas, then the increase in volume on sparking is nearer nine-fold than eight-fold. From this increase in volume and from the relative proportions of hydrogen and carbon monoxide contained in the sparked gases, the unknown mother-substance (*x*) might be imagined to have been a reduction product of some polymer of formaldehyde, of empirical formula perhaps $H_{10}(CO)_4$, formed by the action of hydrogen of great reducing power which, as we shall see, is probably produced during the photolysis. The fact that it was not frozen out at the temperature

of solid carbon dioxide is, however, as remarkable as the inability of liquid air to hold the formaldehyde vapour. It has indeed been suggested to us that the expansion on sparking was merely due to gases driven out of the electrodes. Against this view, in itself not improbable, we would say (*a*) that no appreciable increase in volume was observed when sparking oxygen or nitrogen alone, (*b*) that the increase in volume caused by *one* spark (21·5 divs. becoming 56) was of quite a different order from the expansions observed when, for example, sparking gas containing formaldehyde, and (*c*) that it would be a coincidence if *both* the gases from the electrodes *and* the original gas taken were found, after sparking, to consist simply of hydrogen and carbon monoxide.

The following table contains a summary of the results of this experiment, as far as the gaseous products of reaction are concerned. Volumes are in c.c.

		Vol. formed during expt.	Vol. per hour.	Percentage of total gases.
Fraction (*a*)	H·CHO	0·161	0·0088	0·99
	CO	0·121	0·0066	0·74
	H_2	0·063	0·0035	0·39
	Total	0·345*	0·019	2·12
Fraction (*b*)	CO_2	15·823	0·8656	97·34
	x	0·087†	0·0048	0·54
	Total	15·910	0·870	97·88
Total gases		16·25	0·889	100

* Residual gases not included. † Possible residual gases included.

The formic acid solution after the experiment still contained formaldehyde (or perhaps some less volatile polymer) in comparatively large amounts. On evaporation, whether on the water-bath or in a desiccator over calcium chloride and soda-lime, no trace of solid residue could be found. On the other hand, after evaporation in the desiccator, a distinct ethereal smell was noted. This may possibly have been methyl formate or methyl alcohol, but was not characterised more closely.

Experiment 2. Another portion of 2·40*M*-formic acid was insolated as in the first experiment, but for 3 hours only. The yields, in c.c. per hour, of gaseous products were :

H·CHO, 0·0091; CO, 0·0050; H_2, 0·0040; CO_2, 0·916;
x, not determined exactly, but of the order of 1% of the CO_2.

The general nature of the results is as in Expt. 1, and there is fair quantitative agreement—perhaps as good as could be expected in view of the complex secondary reactions which obviously take place. As before, formaldehyde was detected in the photolyte after the insolation.

Berthelot and Gaudechon assume that frequency has a very

marked effect on the products of this photolysis, the reaction $H{\cdot}CO_2H \longrightarrow H_2O + CO$ occurring in the wave-length region 250—300 μμ, and the reaction $H{\cdot}CO_2H \longrightarrow H_2 + CO_2$ being caused solely by wave-lengths shorter than 250 μμ. We accordingly directed our attention to this matter, using the filter solutions already described (preceding paper).

Experiment 3. A 2·40*M*-solution of formic acid was insolated for 16 hours by quartz–mercury lamp light which had been filtered by passage through 5 mm. of 0·075% Diamond Fuchsin solution, and therefore (apart from red light) was almost monochromatic 365 μμ radiation. No perceptible decomposition occurred, although the extinction coefficient of formic acid for this wave-length is about twice that of oxalic acid, which does undergo slight decomposition.

Experiment 4. The same solution was exposed for 13·64 hours to quartz–mercury lamp light which had passed through a filter of 5 mm. of 0·025% Auramin O (twice as concentrated as was used in the corresponding oxalic acid experiment), the transmission of which was calculated to be:

μμ	313	303	297	290	280
Transmission (%)	6·9	13·5	16·0	13·2	6·3

The gaseous products were fractionated and treated as before. Fraction *a* measured 21 divisions, was 2·8% of the total gases, and appeared to be similar in composition to the previous fractions obtained in the same way. A more definite statement cannot be made, as, on sparking before adding oxygen, the gas only expanded slightly, though definitely, in volume, and was afterwards found to contain carbon dioxide. Clearly, some air had leaked in. Fraction *b* measured 0·401 c.c. at 15°, constituted 97·2% of the total gases, and contained 97·6% of carbon dioxide. The residual 2·4% was not examined. The results of this experiment in respect of carbon dioxide evolution were thus essentially the same as those obtained in the whole light of the lamp, whereas, according to Berthelot and Gaudechon, the light used being free from short wave-length radiation, only carbon monoxide should have been produced.

Mechanism of the Reaction.

The results recorded above indicate that by far the most important product of the photolysis of a 2·4*M*-solution of formic acid, whether by the full light of the quartz–mercury lamp or by the group of lines comprised between 280—313 μμ, is carbon dioxide; that both hydrogen and carbon monoxide are formed at the same time, but only to the extent of about 0·5% of the quantity of carbon dioxide, rather more carbon monoxide than

hydrogen being produced; and that considerable amounts of formaldehyde and of other reduction products of formic acid also result.

The preponderance of carbon dioxide suggests that the main reaction is $H{\cdot}CO_2H \longrightarrow CO_2 + H_2$, but it is necessary to account for the absence of the great proportion of the hydrogen demanded by this equation. We suggest that both its disappearance and the presence of formaldehyde (and probably of reduction products of the latter) can be accounted for by the assumption that the nascent or activated hydrogen molecules, in virtue of their high energy content, are capable of reducing those formic acid molecules with which they collide: $H_2' + H{\cdot}CO_2H \longrightarrow H{\cdot}CHO + H_2O$. As the formaldehyde accumulates, so it becomes available for further reduction in the same way, and the unknown complex gas x in our b-fractions, and also the substance (perhaps the same as x) noted with the ethereal smell, probably arise in this manner.

It may be remarked that, although in the case of oxalic acid photolysis we concluded that the formaldehyde was produced according to the reaction $CO_2' + H_2O \longrightarrow H{\cdot}CHO + O_2$, the same mechanism, though it may well account for some of the formaldehyde produced in the present case, cannot account for all. The quantities are greater, both absolutely and relatively; the simultaneous production of oxygen required by this equation could not have escaped notice (unless, of course, we assume the oxygen itself to be so "activated" on formation as to oxidise formic acid to carbon dioxide and water); and the deficiency in hydrogen would not be accounted for. Another possible mechanism which would account both for formaldehyde production and for hydrogen deficiency is that the primary reactions $H{\cdot}CO_2H \longrightarrow CO_2 + H_2$ and $H{\cdot}CO_2H \longrightarrow CO + H_2O$ proceed at about the same rate, and that the nascent carbon monoxide and hydrogen mutually destroy one another thus: $CO + H_2 \longrightarrow H{\cdot}CHO$. This, however, seemed unlikely. Apart from the necessity of assuming equal probabilities for the two primary decompositions, it was improbable that any but quite a small proportion of nascent carbon monoxide and hydrogen molecules would collide before deactivation had occurred.

There remained then the first suggestion of interaction between molecules of activated H_2' and of formic acid, a suggestion which could be tested very simply by varying the concentration of the formic acid, the molecules of which are assumed to act as acceptors for the H_2' molecules. An increase in its concentration should increase the formaldehyde yield at the expense of the hydrogen, whilst a decrease should have the reverse effect. We therefore carried out an insolation with a more dilute formic acid solution.

Experiment 5. A 0·113*M*-solution was insolated in the usual way by the full radiation of the mercury lamp for 7·75 hours. Owing to an accident, the gases were not completely pumped off. However, two samples were obtained, simply using solid carbon dioxide around the freezing-bulb, and thereby not separating fractions *a* and *b*, although removing water vapour and formic acid. They were measured (using a capillary tube of which one division represented 0·0119 c.c. instead of 0·000547 c.c. as hitherto) and analysed, with the following results:

Sample (i).		Sample (ii).	
CO_2	46 divisions.	CO_2	19 divisions.
CO	11 ,,	CO	2·5 ,,
H_2	68 ,,	H_2	15·3 ,,
		Residue	2·2 ,,
Total	125 ,,	Total	39 ,,

Both samples were sparked after absorption of carbon dioxide but before being analysed for carbon monoxide and hydrogen. In the first case, there was a slight increase in volume (about 7%), and in the second, no perceptible change. Formaldehyde was not detectable in the solution after photolysis.

Owing to the accident referred to, the results are not as completely conclusive as could be wished, but the following points are definitely established. (*a*) The proportion of hydrogen has been enormously increased. The quantity recovered was actually greater than the quantity of carbon dioxide, but that is, of course, due to the greater solubility of the latter—the difference between the compositions of the first and second samples is evidence of this. (*b*) This increase in the production of hydrogen is accompanied by a suppression, complete or nearly so, of formaldehyde formation. (*c*) There is a large increase in the ratio $CO : CO_2$ in the products of photolysis. There seems little doubt then as to the truth of our assumption—the deficiency of hydrogen and the production of formaldehyde are due to one and the same cause. The increase in the carbon monoxide content of the gases suggests, moreover, that the decrease in formic acid concentration has had a similar effect in this case as well, and that, in more concentrated solutions, the primary photolysis $H{\cdot}CO_2H \longrightarrow H_2O + CO'$ is followed by $CO' + H{\cdot}CO_2H \longrightarrow CO_2 + H{\cdot}CHO$. If that be so, the extent of the primary reaction $H{\cdot}CO_2H \longrightarrow H_2O + CO$ can in no sense be estimated from experiments with concentrated formic acid solutions. The relative amounts of hydrogen and carbon monoxide recovered during the present experiment indicate that it occurs to the extent of about one-sixth of the primary reaction $H{\cdot}CO_2H \longrightarrow H_2 + CO_2$.

If it can be assumed (as indeed most of our figures indicate) that the regular and standardised method of evacuation adopted would result in the pumping off on each occasion of a definite fraction of any dissolved gas held in purely *physical* solution, the figures quoted above would indicate that this fraction is 0·775 for the hydrogen and 0·773 for the carbon monoxide, and that there were originally present 87·7 and 14·2 divisions of these gases, respectively. The same assumption in the case of the carbon dioxide would lead to a fraction of 0·59 and a total volume of 78·4 divs. As, however, this gas is more soluble and partly present as H_2CO_3, the fraction removed on each occasion would be less, and, moreover, would fall with successive evacuations; if this be so, an original carbon dioxide volume of 87·7 instead of 78·4 divs. would not be an unreasonable figure to assume.

Energetics.

We determined the extinction coefficients of a 2·25*M*-formic acid solution by means of the spectrometer–thermopile–galvanometer method, using 5 cm. and 5 mm. layers. Our results were as follows ($\log_{10}$; g.-mol.; litre; cm.):

λ in $\mu\mu$ ...	365	313	303	297	290	280
k	0·003	0·006	0·0082	0·010	0·0144	0·024
λ in $\mu\mu$ ...	275	270	265	254	248	
k	0·032	0·041	0·055	0·30	0·85	

Bielecki and Henri (*Compt. rend.*, 1912, **155**, 456) give for $\lambda = 255\mu\mu$ and 245·2 $\mu\mu$, $k = 0{\cdot}25$ and 2·4, respectively.

Using these data, and the results of Expts. 1, 2, and 4, we can calculate approximately, as in the preceding paper, the quantum efficiencies of this reaction for the wave-length regions 254—275 $\mu\mu$ (average value 260 $\mu\mu$) and 280—313 $\mu\mu$ (average value 300 $\mu\mu$). Neglecting any small possible reaction between CO_2' and water, with production of formaldehyde, the quantity of formic acid primarily decomposed is measured by the sum of the carbon monoxide and carbon dioxide formed.

Quantum Efficiency for 300 $\mu\mu$.—The data used were those of Expt. 4. In 13·64 hours, the absorbed energy was

$\mu\mu$	313	303	297	290	280
Ergs $\times 10^{-7}$	1·98	1·84	0·96	0·59	0·81

the total of $6{\cdot}18 \times 10^7$ ergs corresponding to $0{\cdot}94 \times 10^{19}$ quanta of wave-length 300 $\mu\mu$. Fraction b was 0·401 c.c. at 15° = 0·380 c.c. at *N.T.P.* Neglecting the small amount of carbon monoxide (a correction of the order of 0·5—1%) we have

$$\frac{0{\cdot}380 \times 0{\cdot}976 \times 6{\cdot}1 \times 10^{23}}{22400} = 1{\cdot}00 \times 10^{19}$$

as the number of molecules of formic acid decomposed. The quantum efficiency γ_{300} is therefore 1·06.

Quantum Efficiency for 260 μμ.—For this calculation, we took, from Expts. 1 and 2, 0·89 c.c. per hour as the yield of carbon dioxide produced under the standard conditions of insolation. This corresponded to a total of $22{\cdot}78 \times 10^{18}$ molecules. In the same time, $7{\cdot}29 \times 10^{18}$ quanta of light of average wave-length 300 μμ were absorbed. Using the value of $\gamma_{300} = 1{\cdot}06$ just given, this would cause the decomposition of $7{\cdot}73 \times 10^{18}$ molecules, leaving $15{\cdot}05 \times 10^{18}$ to be accounted for. The number of absorbed quanta for the 254—275 μμ spectral region was $5{\cdot}62 \times 10^{18}$ per hour (the centre of gravity being at about 260 μμ and not at 265 μμ, as was the case with oxalic acid). This gives a value for γ_{260} of 2·68.

For wave-lengths between 250 and 300 μμ, therefore, the quantum efficiencies for the primary photolysis of 2·4*M*-formic acid are about 260 times those for 0·6*M*-oxalic acid. On the other hand, they clearly fall much more rapidly for formic acid at longer wave-lengths.

Quantum Efficiency at Lower Concentrations.—It appeared of interest to check the above figures by the data of Expt. 5, taking the sum of the extrapolated volumes of hydrogen (87·7 divs.) and carbon monoxide (14·2 divs.) as a measure of the decomposition of the 0·113*M*-solution in 7·75 hours. One can calculate, as previously, that, during 1 hour, there were absorbed $11{\cdot}13 \times 10^{17}$ quanta of $\lambda = 260$ μμ and $3{\cdot}97 \times 10^{17}$ quanta of $\lambda = 300$ μμ, to which corresponds a total decomposition of $3{\cdot}40 \times 10^{18}$ molecules of formic acid. The corrected volume of carbon monoxide and hydrogen formed per hour is equivalent to $4{\cdot}00 \times 10^{18}$ molecules. If only the hydrogen be counted, the figure is $3{\cdot}45 \times 10^{18}$ molecules. We regard this improved agreement as fortuitous, and the discrepancy between the figures 3·40 and 4·00 as a real one, due to the centre of gravity of the absorbed energy in Expt. 5 lying further in the ultra-violet than in experiments with more concentrated solutions (thus, nearly 80% of the energy absorbed in the 260 μμ region was due to the 254 μμ line). The effect would be that the quantum efficiencies used for calculation would be too low, and hence also the computed yields. We consider that the extent of agreement obtained shows that, within the limits 2·40—0·113*M*, the quantum efficiency in this reaction is independent of concentration, and we further think that it supports the view already put forward on the mechanism of the primary and secondary changes involved in the photolysis.

The evidence of collision between H_2' or CO′ molecules and formic acid molecules, afforded by the production of formaldehyde

and by the difference between the results of Expts. 1 and 5, suggests strongly that the same mechanism is the cause of the value of 2·68 found for γ_{260}. It would seem that the effect of such collisions will depend on the energy content of the activated molecules at the instant of collision. The higher the frequency of the light and the shorter the interval of time between the liberation of the activated molecule and its collision with a formic acid molecule the greater will be this energy content and the higher will tend to be both γ and formaldehyde yield. The value 2·68 for γ_{260} suggests the production of short reaction-chains, presumably resulting from the absorption of the larger quanta comprised in this group. The results of Expts. 1 and 5 suggest that, in the first stages of deactivation, the H_2' and CO′ molecules lose the power of producing formaldehyde by collision with formic acid molecules, whilst still being able to break up the latter (*e.g.* $H_2' + H{\cdot}CO_2H \longrightarrow H_2 + H_2O + CO$). The energy content of a H_2' (or CO′) molecule resulting from decomposition of formic acid by a 300 $\mu\mu$ quantum is, however, not even sufficient to cause decomposition of another formic acid molecule on collision; and this suggests that formaldehyde had not indeed been formed during Expt. 4, and that the absence of an expansion on sparking was not simply due, as we surmised, to an air leak.

Final Discussion.

Even after making full allowances for the differences between the experimental conditions of Berthelot and Gaudechon's work and our own, we find it difficult to reconcile their data and views on the oxalic and formic acid photolyses with ours. Their failure to detect decomposition of oxalic acid solutions by wave-lengths longer than 300 $\mu\mu$ is probably due to the small absorption for these wave-lengths of the thin layers of solution they used. But their statement that formic acid decomposes in two different ways above and below 250 $\mu\mu$, giving carbon monoxide plus water and hydrogen plus carbon dioxide, respectively, is directly in conflict with our own experiments. Nor can we bring into accord with our results their statement that the products of long-continued photolysis of an oxalic acid solution in the full light of the quartz–mercury lamp are solely carbon dioxide and hydrogen, without any formic acid or carbon monoxide. The production of formaldehyde during oxalic acid photo-decomposition is mentioned by them only incidentally, and is not reported as occurring during the photolysis of anhydrous formic acid, although our results with solutions make it probable that it is, at all events, an intermediate product in that case as well.

Possibly Berthelot and Gaudechon in some cases mistook form-

aldehyde vapour for a mixture of carbon monoxide and hydrogen, as we did at the beginning of our work. Very probably their working temperatures were rather high, as seems to have been the case in most of their photochemical work. In such circumstances, the formaldehyde would largely be given off from the oxalic acid solution as vapour, and would undergo photo-decomposition to hydrogen and carbon monoxide, together with some carbon dioxide and methane, as both they (*Compt. rend.*, 1910, **150**, 1690) and von Goldberger (Diss., Karlsruhe, 1915) found. It is significant that methane is mentioned by them as one of the products of photo-decomposition of anhydrous formic acid. Possibly also under their conditions—higher intensities than we used and also probably a greater proportion of shorter wave-length light—considerable formation of the reducing sugars (noted by Baly, Heilbron, and Barker) took place, but was not tested for. In any case, with such differences in experimental conditions, a quantitative comparison of any sort between their results and ours is out of the question—thus it is quite easy to show, from our quantum efficiency, energy distribution, and absorption experiments, that any secondary decomposition of primarily-produced formic acid during our oxalic acid experiments would be quite negligible, whereas it probably did happen in some of their work. The quantitative discrepancies are nevertheless surprising.

With regard to Volmar's calculations, it is only necessary to say that our experiments do not confirm them. He gives 320 and 210—220 μμ as the threshold wave-lengths for oxalic acid and formic acid photolysis, respectively—we find decomposition at 365 and 280—313 μμ, respectively. It may be added that, according to Franck (*Z. Elektrochem.*, 1925, **31**, 350), there is no sound theoretical basis for such calculations.

Summary.

(1) Light of wave-length 250—300 μμ decomposes formic acid according to the two primary reactions, $H{\cdot}CO_2H \longrightarrow CO_2 + H_2'$ and $H{\cdot}CO_2H \longrightarrow CO' + H_2O$, the former probably taking place to the extent of about six times the latter.

(2) If the formic acid solution be sufficiently concentrated, the greater part of the nascent hydrogen and carbon monoxide molecules, more particularly the former, undergo secondary reaction with the formic acid, giving formaldehyde and still more highly reduced products.

(3) The quantum efficiencies for formic acid decomposition in 0·11—2·4*M*-solutions are of the order of 1·0 for 300 and 2·7 for 260 μμ.

(4) The work of Berthelot and Gaudechon on the photolysis of oxalic and formic acids is discussed in the light of the experimental facts here presented.

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CCCLXXXI.—*The Velocity of Saponification of Mono- and Di-substituted Chloro- and Methoxy-derivatives of Ethyl Benzoate.*

By WILLIAM BLAKEY, HAMILTON MCCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH.

THE influence of a single substituent in the benzene nucleus upon the velocities of such reactions as the saponification of esters and of amides, the esterification of acids, and the hydrolysis of substituted benzyl chlorides has been determined, in many cases, by reference to the actual velocity coefficient for a wide variety of substituents. These results show that a substituent may cause (*a*) a very considerable change in the reactivity and (*b*) a certain order of reactivity related to the position it occupies in the nucleus.

In the saponification of amides *p*-nitrobenzamide alone has a higher reactivity than benzamide, and other substituents cause comparatively small changes in the velocity coefficient (Remsen, *Amer. Chem. J.*, 1899, **21**, 340). The esterification of substituted benzoic acids in the presence of a catalyst proceeds much less readily than with benzoic acid itself (Meyer, *Z. physikal. Chem.*, 1897, **24**, 219), whilst esterification in the absence of a catalyst proceeds most readily with the substituted acids (Michael, *Ber.*, 1909, **42**, 317). The velocity of saponification of an ethyl benzoate substituted by a halogeno- or by a nitro-group is higher than for the simple ester, but methyl and methoxyl groups tend to a lowering of the coefficient, whereas in the hydrolysis of substituted benzyl chlorides the methyl group alone raises the velocity, all other substituents depressing it in comparison with the simple chloride.

A consideration of the effects due to the nature and position of a substituent shows that in the saponification of esters and amides and in the esterification of acids, for the methyl group, the halogens and the hydroxyl and methoxyl groups, the order of reactivity is *m*-> *p*-> *o*-; whereas for the nitro-group the order is *p*-> *m*-> *o*-.

In the hydrolysis of the benzyl chlorides, the order of reactivity is *p*-> *o*-> *m*- for all groupings except the nitro- and carboxyl groups, where the order is *m*-> *o*-> *p*-. The influence of an ortho-substituent in benzyl chloride is small compared with the effect of the same substituent in an ester, and if allowance is made for this decrease in the steric factor it would appear that the two reactions are influenced in opposite ways, although it is the same carbon atom that is involved in the reaction.

Reaction velocities when the nucleus contains a second substituent have been determined only in a few isolated cases; thus, Sirks (*Rec. trav. chim.*, 1908, **27**, 237) determined the esterification coefficients for the dinitrobenzoic acids and Olivier (*ibid.*, 1926, **45**, 296) the velocity of hydrolysis of three dibromobenzyl chlorides.

The ionisation constants of certain disubstituted benzoic acids were determined by Ostwald (*Z. physikal. Chem.*, 1889, **3**, 385), and it was noted that this constant could be calculated approximately if the constants for the mono-substituted and the unsubstituted acids were known. This work was extended by Holleman (*Rec. trav. chim.*, 1901, **20**, 361) to the chloronitro- and bromonitrobenzoic acids, the observed and the calculated values being in reasonable agreement except in the cases of the 2-nitro-3-halogenobenzoic acids. In general, acids substituted in the 2 : 3- and 2 : 6-positions have an abnormally high ionisation constant and show the greatest deviation from the calculated value.

Although there appears to be no proportionality between the ionisation constant of an acid and its coefficient of esterification or the saponification of its esters, yet there is a certain parallelism, and it seemed of interest to determine how far it would be possible to calculate the velocity of saponification of a disubstituted ester from the coefficients for the mono-substituted and for the unsubstituted esters.

The substituents chosen were the methoxyl group and chlorine; the first group has but little effect on the ionisation constant of benzoic acid and might be expected to have a small steric factor, whereas chlorine causes a large increase in the ionisation constant of benzoic acid and the steric effect is large.

The reaction was measured in 95 and 70% alcohol–water mixtures at 30°. The choice of solvent rested upon the following considerations : (1) The reaction could be measured up to 75% change in less than 30 hours even with the most stable esters; (2) the violent disturbance of the velocity coefficient due to traces of water gaining access to absolute alcohol would be eliminated; (3) whatever the nature of the ester, the velocity coefficient is least sensitive to effects due to the solvent in 70% alcohol (J., 1922, **121**, 243).

The results show that in 95% alcohol the order of the velocity coefficients for the methoxybenzoic esters is *o*-> *m*-> benzoate> *p*-, whereas in 70% alcohol the order is *m*-> benzoate> *o*-> *p*-. The dimethoxybenzoic esters in 95% alcohol gave the order 2 : 3 > 2 : 5 > 3 : 5 > benzoate > 3 : 4 > 2 : 4, and in 70% alcohol 3 : 5 > 2 : 5 > 2 : 3 > benzoate > 3 : 4 > 2 : 4. The calculated value of the velocity coefficient was determined from an equation of the type :

$$k_{2:4\text{-ester}}/k_{\text{benzoate}} = (k_{2\text{-ester}}/k_{\text{benzoate}}) \times (k_{4\text{-ester}}/k_{\text{benzoate}}).$$

The ratio of the calculated to the observed value of k was 1 : 1·2, within an experimental error of 3% on the velocity coefficient. This result is all the more striking when it is considered that in this case even the *relative* order of the velocity coefficients for the mono-substituted esters changes with a change in the composition of the solvent.

In the case of the chloro-esters, the relative order of the velocity coefficients is *m*-> *p*-> *o*-> benzoate, and for the dichloro-esters, 3 : 5 > 3 : 4 > 2 : 5 > 2 : 4 > 2 : 3 > benzoate, this order being independent of the composition of the solvent. The ratio of the calculated to the observed value of k varied widely.

This difference in behaviour of the dichloro- and the dimethoxy-esters cannot be ascribed solely to steric effects, for if we omit from consideration the 2 : 3-dichlorobenzoic ester (where the steric factor might be supposed to be greatest) the ratio of $k_{\text{obs.}}/k_{\text{calc.}}$ for the other esters still varies over wide limits.

It was thought that this difference in behaviour might possibly be due to the peculiar behaviour of the ortho-substituted chlorobenzoic esters. It has been noted (J., 1922, **121**, 252) that ethyl *o*-chlorobenzoate on saponification, under apparently identical conditions, gave rise to two values for the velocity coefficient; in the present work, similar results have been obtained. Thus in 95% alcohol k was found to be 0·096 and 0·071, in 70% alcohol 0·162 and 0·116. The ethyl esters of the dichlorobenzoic acids having an ortho-substituent also show this peculiarity, since, in 95% alcohol, the 2 : 3-dichlorobenzoate gave 0·23 and 0·157, and in 70% alcohol 0·44 and 0·34. The lower value of k is in each case about 0·7 times the higher value. This difference in values lies well outside the highest experimental errors; it occurs whether ester, alkali, and solvent are taken from the same or from different samples, and, moreover, one value may be obtained three or four times in succession. It is found, however, that no combination of values will yield an approximately constant value for the ratio $k_{\text{obs.}}/k_{\text{calc.}}$

Thus it would appear that in those cases in which the presence of

a substituent causes a large increase in the reactivity of an ester, it is impossible to calculate the velocity coefficient of a di-substituted ester from the coefficients for the mono-substituted and unsubstituted esters.

EXPERIMENTAL.

The chlorobenzoic acids were obtained by the usual methods. The 2 : 3- and 2 : 5-dichlorobenzoic acids were obtained by nitration of *o*-acetotoluidide, separation of the nitroamino-compounds, conversion into the dichlorotoluenes, and oxidation. 3 : 4-Dichlorobenzoic acid was obtained from *p*-acetotoluidide by a similar series of operations. The 3 : 5-dichlorobenzoic acid was prepared by chlorination of *o*-acetotoluidide, hydrolysis, deamination, and oxidation of the resulting dichlorotoluene. Acetanilide was converted into 2 : 4-dichloroacetanilide, which was hydrolysed to the amine, and this was converted into the nitrile and thence into 2 : 4-dichlorobenzoic acid.

The three methoxybenzoic acids, and 2 : 4- and 2 : 5-dimethoxybenzoic acids were obtained by the methylation of the corresponding hydroxy-acids, which were Kahlbaum products. The 2 : 3-dimethoxybenzoic acid was prepared by converting *o*-vanillin into *o*-veratraldehyde and oxidising this product. The oxidation of eugenol methyl ether yielded 3 : 4-dimethoxybenzoic acid, and the oxidation of orcinol dimethyl ether 3 : 5-dimethoxybenzoic acid.

Certain of the hydroxy-acids could be methylated only with great difficulty and with poor yields; in such cases the best results were obtained by dissolving the acid in methyl sulphate and adding drop by drop a concentrated solution of potassium hydroxide with vigorous stirring.

TABLE I.

Ethyl 2 : 4-dichlorobenzoate in 70% alcohol.

$a = 0{\cdot}01314$; $b = 0{\cdot}00667$.

t.	x.	k.
30	0·00146	0·66
45	0·00199	0·65
65	0·00257	0·64
85	0·00308	0·64
105	0·00354	0·65
135	0·00408	0·66
165	0·00447	0·65
205	0·00490	0·64
255	0·00528	0·65
317	0·00568	0·65
	Mean	0·65
	Duplicate	0·65

TABLE II.

Ethyl *o*-methoxybenzoate in 95% alcohol.

$a = 0{\cdot}04625$; $b = 0{\cdot}03333$.

t.	x.	k.
270	0·01330	0·038
390	0·01417	0·037
510	0·01660	0·037
840	0·02185	0·039
960	0·02243	0·037
1120	0·02363	0·036
1240	0·02480	0·037
1360	0·02565	0·037
1480	0·02570	0·034
1590	0·02627	0·035
	Mean	0·037
	Duplicate	0·035

TABLE III.

Ester.	Solvent, 95% alcohol. Limit k.	k.	Solvent, 70% alcohol. Limit k.	k.
Benzoate	0·0265—0·029	0·028	0·102 —0·108	0·105
o-Methoxy-benzoate	0·0355—0·038	0·0365	0·076 —0·079	0·077
m- ,, ,, ...	0·0350—0·0365	0·035	0·122 —0·129	0·126
p- ,, ,, ...	0·0067—0·0059	0·0063	0·022 —0·024	0·023
o-Chloro- ,, ...	0·094 —0·098	0·096	0·111 —0·119	0·116
	0·069 —0·073	0·071	0·158 —0·164	0·162
m- ,, ,, ...	0·181 —0·192	0·187	0·73 —0·75	0·74
p- ,, ,, ...	0·112 —0·122	0·116	0·38 —0·42	0·40

TABLE IV.

Ester.	Solvent, 95% alcohol. Limit k.	k.	Solvent, 70% alcohol. Limit k.	k.
2 : 3-Dimethoxy-benzoate	0·057 —0·065	0·061	0·106 —0·115	0·110
2 : 4- ,, ,,	0·0081—0·0088	0·0084	0·0181—0·0200	0·019
2 : 5- ,, ,,	0·055 —0·060	0·057	0·122 —0·130	0·122
3 : 4- ,, ,,	0·0100—0·0107	0·0102	0·037 —0·041	0·038
3 : 5- ,, ,,	0·043 —0·047	0·046	0·172 —0·183	0·175
2 : 3-Dichloro- ,,	0·150 —0·160	0·157	0·33 —0·36	0·34
2 : 4- ,, ,,	0·202 —0·214	0·206	0·64 —0·655	0·65
2 : 5- ,, ,,	0·415 —0·425	0·42	0·99 —1·09	1·04
3 : 4- ,, ,,	0·55 —0·59	0·57	1·90 —2·00	1·95
3 : 5- ,, ,,	1·48 —1·57	1·52	4·05 —4·25	4·20

TABLE V.

Ester.	95% Alcohol. $k_{obs.}$	$k_{calc.}$	$k_{obs.}/k_{calc.}$	70% Alcohol. $k_{obs.}$	$k_{calc.}$	$k_{obs.}/k_{calc.}$
Ethyl dimethoxybenzoates.						
2 : 3-	0·061	0·046	1·33	0·110	0·093	1·18
2 : 4-	0·0084	0·0082	1·02	0·019	0·017	1·12
2 : 5-	0·057	0·046	1·24	0·122	0·093	1·31
3 : 4-	0·0102	0·0079	1·29	0·038	0·028	1·35
3 : 5-	0·046	0·044	1·05	0·175	0·151	1·16
Ethyl dichlorobenzoates.						
2 : 3-	0·157	0·474	0·33	0·34	0·817	0·42
2 : 4-	0·206	0·295	0·71	0·65	0·44	1·47
2 : 5-	0·42	0·474	0·89	1·04	0·817	1·27
3 : 4-	0·57	0·775	0·72	1·95	2·82	0·70
3 : 5-	1·52	1·25	1·22	4·20	5·21	0·81

The acids were all recrystallised from water or from aqueous alcohol until a constant melting point was obtained. They were converted into their ethyl esters by the usual method; liquid esters were twice distilled in a vacuum, and the solid esters were crystallised from aqueous alcohol.

The alcohol–water mixtures and the standard solutions of potassium hydroxide, acid, and ester were prepared in the usual manner. The experiments were carried out at $30° \pm 0·05°$. In the tables, time, t, is shown in minutes. "Limit k" represents the extreme values obtained in two determinations, and k the mean value of both determinations.

In calculating the value of k the lower velocity coefficient for ethyl *o*-chlorobenzoate has been employed.

Summary.

1. The velocities of saponification of six mono-substituted and ten di-substituted benzoic esters have been determined in two ethyl alcohol–water mixtures.

2. It has been shown that both for the chloro- and for the methoxy-esters the *m*-substituted compounds are the most reactive, except in one case.

3. The values of k found for the dimethoxy-esters bear a definite relation to those of the monomethoxy-esters, whereas in the case of the dichloro-esters this relationship is not observed.

4. It is shown that the relative order of the velocity coefficients for the monomethoxy-esters is altered by a change in the composition of the solvent.

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CAMBRIDGE. [*Received, July 23rd,* 1926.]

CCCLXXXII.—*The Basic Sulphate of Copper. A Reply.*

By HUBERT THOMAS STANLEY BRITTON.

FOWLES (this vol., p. 1845) claims to have found "the cause of most of the perplexing anomalies" relating to the numerous basic sulphates of copper which have been reported, but in so doing he has added two more to their number, although he has not advanced any satisfactory proofs of their individualities. It is not justifiable to call any basic substance a "compound" until its fixity of composition and conditions of existence have been ascertained. Constancy of composition may be only apparent owing to the reproduction of some essential condition during the formation of the precipitate, *e.g.*, the hydrogen-ion concentration. Fowles's paper contains many unsubstantiated statements, especially in regard to the importance and application of the phase rule to the study of basic salts. He claims to have isolated a new basic sulphate, $2CuSO_4,Cu(OH)_2,4H_2O$, by boiling a saturated copper sulphate solution "in presence of solid copper sulphate," or "from solutions not fully saturated," and he states that the salt is "therefore stable

over a small range of temperature and concentration." It is difficult to understand how the composition of a precipitate, formed in such concentrated solutions, could be determined, seeing that it is decomposed on treatment with water. Again, the product, $5CuSO_4,9Cu(OH)_2$, is stated to be formed by boiling for a short time solutions either of copper sulphate or of copper sulphate to which sodium nitrite has been added, whereas if the boiling be prolonged $CuSO_4,2Cu(OH)_2$ is obtained, a substance which Fowles maintains to be " the solid phase which is in equilibrium with the acid of hydrolysis in a solution of copper sulphate."

During recent years four attempts have been made to ascertain which of the many recorded basic sulphates are actual compounds by a study of the relevant section of the ternary system $CuO–SO_3–H_2O$. Three of these attempts were made at 25° by Bell and Taber (*J. Physical Chem.*, 1908, **12**, 171), Young and Stearn (*J. Amer. Chem. Soc.*, 1916, **38**, 1947; also at 37·5° and 50°), and the author (J., 1925, **127**, 2796). In the first two studies, somewhat inert substances were used which could only attain equilibrium slowly and with difficulty, and it is doubtful whether true equilibrium was ever attained. In Bell and Taber's work, however, one Schreinemakers tie-line passes quite close to the point corresponding to $4CuO,SO_3,4H_2O$. Young and Stearn made complete analyses, which were not always concordant, of the unwashed solid phases and of the copper content of the liquid phases. Fowles, disputing their results for the solid phases, has recalculated their compositions from the change in concentration of the liquid phases, and considers the results to afford valid evidence of the existence of $CuSO_4,2Cu(OH)_2$, in spite of the fact that the actual analytical data give values ranging from 1·28 to 1·84 mols. of $Cu(OH)_2$ to each mol. of $CuSO_4$. Fowles refers to Young and Stearn's analyses of their so-called solid phases as being vitiated probably owing to the " employment of an unsound analytical procedure," but he regards the analyses of the liquid phases as showing " the high degree of accuracy of the experimental work." It is obvious that much of the difference was due to the fact that Young and Stearn regarded the " rests " as the solid phases, but throughout Fowles's paper it appears that he has done the same thing, especially where concentrated solutions and unstable salts were involved. As stated in the author's paper, the precipitate, $4CuO,SO_3,4H_2O$, formed when alkali (not exceeding 0·75 equiv.) is added to a dilute solution of copper sulphate with continuous shaking, can easily be washed free from impurities, and there is no " danger of forming compounds of the foreign metal " (Fowles, pp. 1852—3). The author has always obtained this salt in a non-gelatinous state,

and never in the gelatinous state mentioned by Fowles. If, however, the alkali is added without the necessary precautions being taken, a gelatinous precipitate of copper hydroxide retaining appreciable amounts of sulphate will be obtained, and may sometimes fortuitously contain CuO and SO_3 in the ratio 4 : 1. In the author's experiments, equilibrium was rapidly established through the use of more reactive substances than had been employed hitherto, *viz.*, sulphuric acid, moist basic sulphate, and moist hydrated copper oxide, and the quantities used were so adjusted that the amounts of solid phases were as small as possible in order to ensure that they should enter completely into equilibrium. In the opinion of the author, there is no doubt that the analyses given actually represent states of true equilibrium. It should scarcely be necessary to remark that the compositions of the liquid and solid phases at the final equilibrium are quite independent of the substances used, whether they be copper oxide, which has been ignited or not, or copper hydroxide; the choice of substances affects only the time required for equilibrium. Fowles, however, attempts to harmonise the conflicting results of Young and Stearn and of Bell and Taber by making such unjustifiable assumptions and, moreover, states that the substances used by the author were such as to make it "impossible for the highly stable intermediate compound $CuSO_4,3Cu(OH)_2$ to pass into the final stable $CuSO_4,2Cu(OH)_2$ salt." He seems to have overlooked the fact that the present author also used partly dehydrated copper hydroxide in some experiments instead of the basic sulphate (*loc. cit.*, p. 2800), and again in every case the solid phase in equilibrium with copper sulphate solution as the liquid phase was $CuSO_4,3Cu(OH)_2,H_2O$. Had Fowles's contentions concerning reactions between copper hydroxide and copper sulphate solutions been correct, the use of hydrated copper oxide should have had some effect on the kind of basic salt obtained. Fowles states (p. 1851) that when "copper hydroxide is added to a solution of copper sulphate there is a concurrence of reactions : the neutralisation of the acid of hydrolysis with the precipitation of the 1 : 2 salt, the formation of the 1 : 3 salt by direct union, the change of the 1 : 2 and 1 : 3 salts into less soluble and less reactive forms, and the conversion of the 1 : 3 salt into the 1 : 2 salt by the action of copper sulphate." The whole of this statement is advanced without any supporting evidence. Fowles gives no data to show that solubility variations take place, and moreover (p. 1850) he even disproves the statement that the 1 : 3 salt passes into the 1 : 2 salt by the action of copper sulphate under ordinary conditions, for he admits that "all attempts to detect any change in composition

when the 1 : 3 salt has been left in contact with cold solutions have failed." If it were likely that the neutralisation of the acid of hydrolysis would give rise to a basic salt different from that produced by the interaction with copper sulphate, the degree of hydrolysis of copper sulphate solutions is so very small that the proportion of basic salt due to that reaction would be too small for detection by the ordinary methods of chemical analysis.

Instead of accepting the evidence as to the composition of the basic sulphate given by the pencil of tie-lines as a whole in the author's phase-rule diagram, Fowles has taken exception to that afforded by the two corresponding to the two most concentrated liquid phases because, when drawn on a large scale, they do not intersect at the point $4CuO,SO_3,4H_2O$. One line passes almost through this point and the other lies at a distance of about a 1% division from it; when it is remembered that such a divergence is caused by an error of much less than 1% in the analysis of the "rest," it will be obvious that the source of the error most probably lies in the experimental method, one cause being the slight evaporation which takes place during the preparation of the "rest" for analysis. Had $CuSO_4,2Cu(OH)_2$ been a basic salt stable, as Fowles seems to think, in some concentrations of copper sulphate solution, then this would have been indicated by a pencil of tie-lines.

Many of the so-called basic salts containing a larger proportion of SO_3 appear to have been obtained from concentrated solutions, *e.g.*, $5CuO,2SO_3,xH_2O$ (Sabatier, *Compt. rend.*, 1897, **125**, 101; Fowles, *loc. cit.*, p. 1854), and this was shown by the author (*loc. cit.*, p. 2802) to be accounted for by mother-liquor adhering to the solid phase. The "rests" corresponding to the liquid phases containing 3·17 and 7·17% CuO were freed as far as possible from adhering liquor by suction, and yet the former contained 0·314 mol. of SO_3 and the latter, 0·423 mol. of SO_3 to each mol. of CuO.* The composition of the former "rest" happens to agree roughly with $3CuO,SO_3$, and the latter with $5CuO,2SO_3$, which both Sabatier and Fowles have considered to be a definite individual. There is no reason to believe that $CuSO_4,2Cu(OH)_2$ is a compound stable at 25° as stated by Fowles, even although a substance having approximately that composition may occur in nature, *viz.*, antlerite.

The fourth paper dealing with the phase-rule study of basic copper sulphate is that by Bell and Murphy (*J. Amer. Chem. Soc.*, 1926, **48**, 1500), who have worked out the 100°-isotherm and have

* The author's thanks are due to Mr. Fowles for directing attention to the fact that the latter "rest" contained 0·423 mol. of SO_3, and not 0·314 mol., which was misplaced in Table I. This, however, does not detract from the argument, as Fowles suggests, but, on the contrary, strengthens it.

found that the only basic sulphate which exists in stable equilibrium at that temperature is the one which the author found at 25°. Fowles states that Bell and Murphy have mistaken the "metastable" * $CuSO_4,3Cu(OH)_2,H_2O$ for the "final equilibrium product," and asserts that "equilibrium was never attained and the statement that the 1 : 3 compound [$CuSO_4,3Cu(OH)_2$] is the basic salt stable at 100° is not correct." As pointed out by Fowles, the method adopted by Bell and Murphy in arriving at the composition of the solid phases is open to objection, for had a basic salt been formed which is decomposed by water, washing before analysis would have given rise to erroneous results, although it is scarcely probable that washing would have been so protracted as to cause the complete transformation into $CuSO_4,3Cu(OH)_2$ in every case shown by Bell and Murphy's figures.

In conclusion, it appears from the phase-rule studies at 25° and 100° that the only basic sulphate of copper which has any real claim to be regarded as a "compound" at these temperatures is $4CuO,SO_3,4H_2O$. There is much evidence for the belief that the same statement holds for intermediate temperatures.

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SOUTH KENSINGTON. [*Received, August 16th*, 1926.]

CCCLXXXIII.—*Acid and Salt Effects in Catalysed Reactions. Part II. The Minimum Reaction Velocities for Acid–Salt Mixtures.*

By HARRY MEDFORTH DAWSON and NORMAN CECIL DEAN.

IT was shown by Dawson and Carter (this vol., p. 2282) that the catalytic effects produced by acids, or by mixtures of acids with the corresponding salts, can be satisfactorily interpreted on the view that catalytic activity is exhibited not only by the hydrogen and hydroxyl ions, but also by the undissociated acid molecule and the acid ion. For the reaction between acetone and iodine in dilute aqueous solution, the various velocity coefficients in the general equation

$$v = k_h[H]^+ + k_a[A]^- + k_m[HA] + k_{OH}[OH]^- \quad . \quad . \quad (1)$$

were evaluated from experiments with acetic acid and with monochloroacetic acid.

* Fowles gives no proof why $CuSO_4,Cu(OH)_2,H_2O$ is to be regarded as a "metastable solid phase" and $CuSO_4,2Cu(OH)_2$ as the stable phase; if the former were metastable to the latter, then it would have a greater solubility. Fowles states that both are "insoluble," but gives no data regarding the actual solubilities.

The observations made with acid–salt mixtures of the type C . HA + x . MA, in which the concentration (C) of the acid is constant, whilst that of the corresponding salt (x) is varied, show that with increasing salt concentration the reaction velocity falls, passes through a minimum, and then increases in a linear manner.

The object of this paper is to discuss the form of the velocity curve for mixtures of this type, and the relations which characterise the mixture for which the reaction velocity has a minimum value, and, further, to show that these are in close agreement with actual experiments. The observations have reference to acetic acid–sodium acetate mixtures, for which the concentration of the hydroxyl ion is so small that its effect can be entirely ignored.

In these circumstances, equation (1) may be written

$$v = v_h + v_a + v_m = k_h[\mathrm{H}]^+ + k_a[\mathrm{A}]^- + k_m[\mathrm{HA}] \quad . \quad . \quad (1a)$$

and, on the assumption that the acid HA conforms to the requirements of the mass law, $[\mathrm{A}]^-$ may be replaced by $K(C - [\mathrm{H}]^+)/[\mathrm{H}]^+$, and [HA] by $C - [\mathrm{H}]^+$. Equation (1a) then becomes

$$v = (k_h - k_m)[\mathrm{H}]^+ + k_aKC/[\mathrm{H}]^+ + k_mC - k_aK \quad . \quad . \quad (2)$$

the fourth term in which is of a negligibly small magnitude. Differentiating (2) we have

$$dv/d[\mathrm{H}]^+ = k_h - k_m - k_aKC/[\mathrm{H}]^{+2} \quad . \quad . \quad . \quad (3)$$

and, since $dv/d[\mathrm{H}]^+ = 0$ when the reaction velocity is a minimum, we obtain

$$[\mathrm{H}]_i^+ = \sqrt{k_aKC/(k_h - k_m)} \quad . \quad . \quad . \quad . \quad (4)$$

where $[\mathrm{H}]_i^+$ denotes the hydrogen-ion concentration of that acid–salt mixture for which the reaction velocity is a minimum. This mixture will be shown to be of considerable significance in the correlation of the experimental observations and will be designated for convenience as the *M.V.* mixture. According to the above equation, the hydrogen-ion concentration of the *M.V.* mixture depends on the catalytic coefficients of the hydrogen and acid ions, on the dissociation constant of the acid, and on its concentration.

If the value of $[\mathrm{H}]_i^+$ given by equation (4) is substituted in equation (2), we obtain the following expression for the minimum reaction velocity v_i, the last term in (2) being neglected :

$$v_i = (k_h - k_m)\sqrt{k_aKC/(k_h - k_m)} + k_aKC\sqrt{(k_h - k_m)/k_aKC} + k_mC$$
$$= 2\sqrt{(k_h - k_m)k_aKC} + k_mC \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In this equation, the first term corresponds with the sum of the velocities due to the hydrogen and acid ions, and it is evident that the *M.V.* mixture is characterised by the relation :

$$(v_h)_i = (v_a)_i = \sqrt{(k_h - k_m)k_aKC} \quad . \quad . \quad . \quad (6)$$

where $(v_h)_i$ and $(v_a)_i$ denote the partial velocities due to the hydrogen and acid ions at the inversion point which corresponds with the minimal velocity.

If each side of equation (3) is multiplied by $[H]^+$, we obtain

$$dv/d \log [H]^+ = (k_h - k_m)[H]^+ - k_aKC/[H]^+ \quad . \quad . \quad (7)$$

from which it follows that the curve obtained by plotting velocity against log $[H]^+$ or against p_H should be symmetrical with reference to the point at which the hydrogen-ion concentration has the value $[H]^+ = \sqrt{k_aKC/(k_h - k_m)} = [H]_i^+$, *i.e.*, with reference to the point corresponding with the *M.V.* mixture.

This may be shown more clearly in the following manner. If v_1 and v_2 be the reaction velocities for mixtures of hydrogen-ion concentrations $[H]^+_1$ and $[H]^+_2$, respectively, then

$$v_1 = (k_h - k_m)[H]_1^+ + k_aKC/[H]_1^+ + k_mC$$
$$v_2 = (k_h - k_m)[H]_2^+ + k_aKC/[H]_2^+ + k_mC$$

and if $v_1 = v_2$, then

$$(k_h - k_m)[H]_1^+ + k_aKC/[H]_1^+ = (k_h - k_m)[H]_2^+ + k_aKC/[H]_2^+$$

and, on rearranging the terms, we obtain

$$[H]_1^+ . [H]_2^+ = k_aKC/(k_h - k_m) = [H]_i^{+2} \quad . \quad . \quad (8)$$

which may be written in the form

$$(p_H)_1 + (p_H)_2 = 2(p_H)_i \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

According to this, the p_H value of the *M.V.* mixture is the arithmetic mean of the p_H values of any pair of solutions of the constant-acid series for which the reaction velocities are equal.

With the object of testing the relations which have been derived above, measurements have been made of the rate of interaction of iodine with acetone under the catalytic influence of mixtures belonging to the series $0{\cdot}05N$-$CH_3{\cdot}CO_2H + xN$-$CH_3{\cdot}CO_2Na$.

The results are represented by the continuous curve in the diagram, in which the reaction velocities obtained for the various mixtures are plotted against the p_H values, which are derived from the mass action equation:

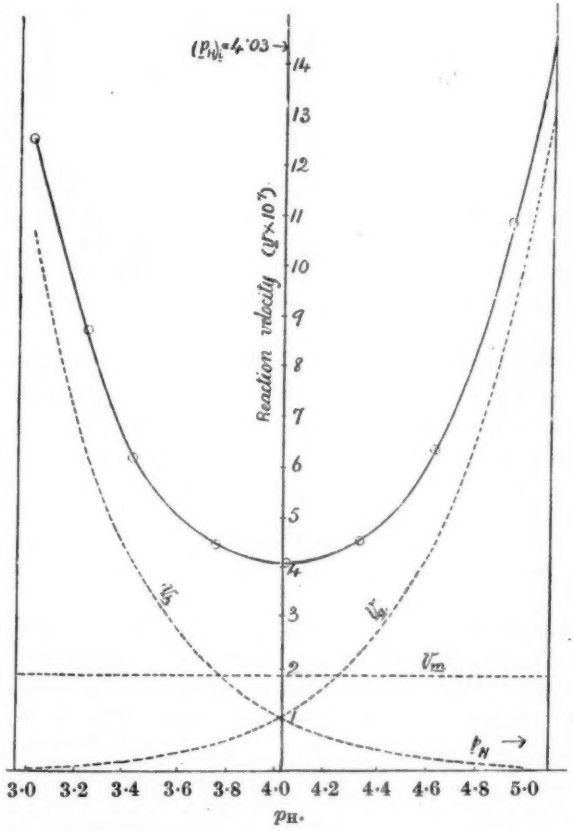
$$p_H = \log 1/K + \log (x + [H]^+)/(C - [H]^+).$$

The dotted curves represent the calculated partial velocities due to the hydrogen ion and the acid ion respectively; the dotted horizontal line represents the velocity due to the undissociated acid. Summation of the dotted curves corresponds with the continuous curve.

Anticipating the suggestion that the required p_H data might have been obtained by direct hydrogen-potential measurements, it may be pointed out that such is not the case. Electrometric and

other thermodynamic methods in their application to electrolytes provide data which have reference to the mean activities of the positive and negative ions and not to the individual activities of these as separate entities. Furthermore, it may be added that there is substantial evidence in our results, not only for the view that salts are completely ionised, but also that catalytic activity is

FIG. 1.



directly proportional to the volume concentration of the molecular or ionic catalyst concerned, and has no apparent connexion with thermodynamic activity. In support of this statement, attention may be directed to the results obtained for the catalytic activity of the acetate ion in experiments with mixtures 0·1*N*-$CH_3 \cdot CO_2H$ + *x*N-$CH_3 \cdot CO_2Na$ at salt concentrations so large that the catalytic effect of the hydrogen ion may be left out of account.

In Table I, cols. 1 and 2 give respectively the concentration of

the sodium acetate and the observed velocity; col. 3 gives the velocity diminished by that due to the undissociated acid, *i.e.*, the velocity v_a due to the acetate ion. Col. 4 gives the ratio of this velocity to the salt concentration (x) and col. 5 the ratio to αx, where α is the conductivity ratio Λ/Λ_∞. The data refer to a concentration of acetone = 20 c.c. per litre.

TABLE I.

x.	$v_{obs.} \cdot 10^6$.	$v_a \cdot 10^6$.	$v_a \cdot 10^6/x$.	$v_a \cdot 10^6/\alpha x$.
0·1	0·60	0·45	4·50	5·77
0·2	1·04	0·89	4·45	6·10
0·3	1·51	1·36	4·53	6·57
0·4	1·95	1·80	4·50	6·82
0·5	2·45	2·30	4·60	7·30
1·0	4·6	4·45	4·45	8·40

The constancy of the numbers in col. 4 affords strong support for the view that the activity of the acid ion is simply proportional to its concentration and that the salt is fully ionised.

In accordance with evidence of this kind, the concentration of the anion in the formula employed for the calculation of p_H has been made equal to $x + [H]^+$.

On referring to the diagram, it will be observed that the velocity–p_H curve is quite symmetrical with respect to the point which corresponds with the *M.V.* mixture. The degree of symmetry may be judged from the data in Table II, in which the p_H values for pairs of solutions which are equally active as catalysts are recorded under $(p_H)_1$ and $(p_H)_2$. These values are those read from a large-scale plot on which horizontal lines were drawn for the series of reaction velocities shown under v in cols. 1 and 4. In accordance with equation (8*a*) the arithmetic mean of these p_H values should be equal to a constant which represents the value of $(p_H)_i$. It will be seen that the actual mean values are very nearly constant and that the p_H value of the *M.V.* mixture for the series 0·05*N*-$CH_3 \cdot CO_2H$ + x*N*-$CH_3 \cdot CO_2Na$ is equal to 4·03. The value of $[H]_i^+$ derived from the equation $[H]_i^+ = \sqrt{k_a K C(k_h - k_m)}$, using the values of k_h, k_a, and k_m recorded by Dawson and Carter (*loc. cit.*), is $[H]_i^+ = 0{\cdot}0_4967$, whence $(p_H)_i = 4{\cdot}012$ in close agreement with the value derived from the velocity curve.

TABLE II.

p_H Values of catalytically equivalent mixtures.

$v \cdot 10^6$.	$(p_H)_1$.	$(p_H)_2$.	$\frac{1}{2}[(p_H)_1 + (p_H)_2]$.	$v \cdot 10^6$.	$(p_H)_1$.	$(p_H)_2$.	$\frac{1}{2}[(p_H)_1 + (p_H)_2]$.
50	3·63	4·43	4·03	90	3·22	4·84	4·03
60	3·46	4·59	4·025	100	3·16	4·90	4·03
70	3·36	4·70	4·03	110	3·10	4·96	4·03
80	3·28	4·78	4·03	120	3·04	5·01	4·025

Amongst the pairs of catalytically equivalent solutions, the one which includes the pure acid (no salt) is of particular interest. If $[H]_0^+$ and $[H]_s^+$ denote the hydrogen-ion concentrations of the pure acid and of the catalytically equivalent acid–salt mixture, then according to equation (8), $[H]_0^+[H]_s^+ = k_a KC/(k_h - k_m)$, and from the mass law $[H]_0^+ = \sqrt{K(C - [H]_0^+)}$, or, approximately, $[H]_0^+ = \sqrt{KC}$. Combination of these equations leads to the relation

$$[H]_s^+ = k_a\sqrt{KC}/(k_h - k_m) \quad . \quad . \quad . \quad . \quad (9)$$

The value of $[H]_s^+$ given by this equation for the acid–salt mixture which has the same catalytic activity as 0·05*N*-acetic acid is $0{\cdot}0_598$, whilst the value derived from the curve in the diagram is $0{\cdot}0_594$.

Since k_m is very small compared with k_h in the case of weak acids, $k_h - k_m$ may be replaced by k_h. The equations for the hydrogen-ion concentration and the reaction velocity characteristic of the *M.V.* mixture then become:

$$[H]_i^+ = \sqrt{k_a KC/k_h} \text{ and } v_i = 2\sqrt{k_h k_a KC} + k_m C.$$

In postponing the discussion of relations in which the minimum reaction velocity v_i is involved, it may be pointed out that the degree of accuracy now attainable in the measurement of the reaction velocities is very much greater than that which characterised some of the earlier measurements. Further work, in which attention is being directed to the precise determination of the catalytic coefficients and the minimum reaction velocity, is in progress.

Experimental.

The acetone was purified by treatment with sodium iodide, and the acetic acid by the chromic acid method described by Orton and Bradfield (J., 1924, **125**, 960). The velocity measurements at 25° were made with solutions containing 50 c.c. of acetone per litre and the original concentration of the iodine was approximately 0·003*M*.

Blank experiments without acetone showed that the loss of iodine was within the limits of experimental error.

In deriving the initial velocity from the actual speed of the auto-catalysed reaction, the usual procedure was followed. Whilst in the presence of little or no salt the auto-catalytic effect is very appreciable, it may be noted that in presence of larger quantities of salt the buffer action of the latter tends to reduce very greatly the auto-catalytic effect.

The initial velocities (mols. per litre per minute) actually obtained in the experiments are recorded in Table III, which shows also

the salt concentration (x), the hydrogen-ion concentration $[H]^+$, and the corresponding value of p_H.

TABLE III.

x	0·001	0·002	0·005	0·01	0·02	0·04	0·06	0·08	0·16
$[H]^+ . 10^4$.....	9·53	5·79	3·85	1·78	0·916	0·463	0·232	0·116	0·058
p_H	3·02	3·24	3·41	3·75	4·04	4·33	4·63	4·94	5·24
$v . 10^6$	1·250	0·870	0·620	0·450	0·412	0·456	0·635	1·040	1·810

Summary.

The significance of the reaction velocity minimum for acid–salt mixtures of the type C . HA + x . MA is discussed.

Equations are derived connecting the hydrogen-ion concentration and the reaction velocity characteristic of the minimum velocity (*M.V.*) mixture with the catalytic coefficients for the hydrogen ion, the acid ion, and the undissociated acid.

It is shown that, for a given acid concentration, catalytically equivalent solutions are those for which the product of the hydrogen-ion concentrations is constant and equal to the square of the hydrogen-ion concentration of the *M.V.* mixture; in other words, that the velocity–p_H curve is symmetrical with respect to the *M.V.* point.

Evidence is adduced in support of the view that salts in aqueous solution are completely ionised, and that the catalytic activity of a catalyst is proportional to its concentration and has no apparent connexion with the thermodynamic activity.

THE UNIVERSITY, LEEDS. [*Received, September 4th*, 1926.]

CCCLXXXIV.—*The Periodic Electrochemical Passivity of Iron, Cobalt, Nickel, and Aluminium.*

By ERNEST SYDNEY HEDGES.

SHORTLY after it had been recognised that iron could assume the passive state, the remarkable observation was made that under certain conditions pulsations are set up, the iron behaving as though it were alternately active and passive; the literature contains many references to this periodic phenomenon which obtains both for the passivity induced by chemical reagents (*e.g.* nitric acid) and for that caused by anodic polarisation.

The results of a study of other periodic electrolytic systems (this vol., pp. 1533, 2580) have now been applied to those metals which readily assume the passive state.

Experimental.

Details of the experimental methods are given in preceding papers (*locc. cit.*). In brief, solutions at 20° were electrolysed with a platinum cathode and an anode of the metal under investigation, readings of the *P.D.* between the electrodes being taken while the current density was being progressively increased. The metals used were all of electrolytic origin and had been rolled into sheets, roughly 0·5 mm. thick. The portion of metal immersed measured 2×3 cm. The metals were cleaned in hydrochloric acid and then in water immediately before use.

Iron Anode.

Experiments in Sulphuric Acid Solutions.—In 100, 80, and 60% * solutions a low *C.D.* was sufficient to cause the *P.D.* to rise to a high value, oxygen being evolved. The whitish appearance of the anode suggested the formation of a film of anhydrous ferrous sulphate. In a 40% solution at a *C.D.* of 160 milliamp./cm.^{2}, the *P.D.* rose from 1·2 to 3·2 volts and oxygen was evolved. Thereafter, the *P.D.* oscillated continuously between 1·1 and 3·3 volts, in periods of 50 seconds. At the lower value of *P.D.* hydrogen was evolved; this ceased as the *P.D.* rose and then gave place to oxygen evolution; during the next fall of *P.D.* the oxygen evolution ceased and slow hydrogen evolution was reinstated. Immediately before the evolution of oxygen a white film could be observed to sweep up the anode. The iron was permanently in the passive state at current densities greater than 250 milliamp./cm.^{2}, and permanently active when the *C.D.* was below 160 milliamp./cm.^{2}.

If the iron was removed from the solution when in its high-potential state, the high *P.D.* persisted on plunging it back again; but if in the meantime the iron was dipped into water it was found to be active on plunging it back into the solution. It is concluded that in these solutions the iron becomes enveloped in a resistant film of anhydrous ferrous sulphate, which is much less soluble in strong solutions of sulphuric acid than in water. It was found also that the passivity obtained in the 100, 80, and 60% solutions was removable by immersing the electrode in water.

In weaker solutions of sulphuric acid, the passivity seems to be quite different. In 10% solution, great difficulty was experienced in inducing passivity, and it was found best to complete the circuit before immersing the anode, so that the initial *C.D.* was very high. By breaking the circuit momentarily, the iron became active,

* See footnote (this vol., p. 2584) for convention as to expression of concentrations throughout this paper.

but, with an increase of current, it again became passive. Thus, with a *C.D.* of 420 milliamp./cm.^{2} the *P.D.* oscillated continuously between 1·5 and 3·3 volts, in periods of 40 seconds. No gas was evolved during the active state of the metal, but oxygen evolution occurred while the metal was in the passive state. In this case, however, the anode was lustrous during the passive periods but acquired a dull, dark grey film during the active periods. Each time passivity set in, the film peeled off and subsequently dissolved in the solution. Evolution of oxygen then ensued, beginning at the lowest part of the electrode, up which the passive state rapidly travelled until the whole of the metal was evolving oxygen. At the end of the period, the oxygen evolution ceased and the metal slowly acquired its grey film, which again peeled off at the next period of oxygen evolution.

In 5% sulphuric acid solution, the precaution mentioned above was still more necessary to secure passivity of the iron; continuous oscillations between 2·4 and 4·0 volts, having a period of 30 seconds, were obtained with a *C.D.* of 850 milliamp./cm.^{2}. The film in this case did not peel off, however, but apparently dissolved, uncovering the lustrous surface.

Closer observation showed that the film is completed just before the *P.D.* rises, then oxygen is evolved, and the film disappears: it does not seem to be an attribute of the active metal, but rather a transitional state between the active and passive states.

Experiments in Nitric Acid Solutions.—In 100% nitric acid, the iron became passive before the current was started. In a 90% solution, the reaction was very vigorous, but the metal could be rendered passive by adopting the device described for the more dilute sulphuric acid solution: passivity then spread from the first point of contact over the whole electrode. Although this solution did not cause passivity, yet it did not activate the passive metal, and on disconnecting the circuit the metal remained permanently passive. In 60% nitric acid, the behaviour was similar, except that on breaking the circuit the iron dissolved with great vigour.

Periodic passivity occurred in 40 and 20% solutions, the *P.D.* oscillating between 1·6 a..d 3·4 volts. The metal had a brown-coloured surface at the low potential and was bright during the passive periods, when oxygen was evolved. The *C.D.* used for the 20% solution was 1800 milliamp./cm.^{2}, and the periods succeeded each other at intervals of 10 seconds. In 10, 2, and 1% solutions passivation took place more readily, but did not become periodic.

Experiments in Phosphoric Acid Solutions.—In 5% orthophosphoric acid, iron became passive at a *C.D.* of 50 milliamp./

cm.^{2}, the *P.D.* rising from 2·2 to 3·8 volts. Oscillations of the potential between 3·65 and 3·85 volts followed, at intervals of 3 minutes. At a slightly higher *C.D.* the metal was permanently passive, whilst it remained active at *C.D.*'s below 50 milliamp./cm.^{2}.

Experiments in Other Solutions.—In solutions of caustic soda or of potassium cyanide iron became passive at the lowest *C.D.*'s, whilst in hydrochloric acid solutions the highest available *C.D.* did not induce the passive state. In solutions of ammonium sulphate or sodium sulphate, the main product was ferrous hydroxide, which fell continuously from the anode. Although at higher *C.D.*'s passivity set in, the anode remained passive until the circuit was broken, and an intermediate oscillating condition was not realised.

Cobalt Anode.

Experiments in Sulphuric Acid Solutions.—In 100 and 80% sulphuric acid, a brown film readily formed over the anode and oxygen was evolved. Periodicity was observed in 50, 40, 30, 25, 20, 15, 10, 5, and 1% solutions, and the effect was far more striking than in the corresponding experiments with iron. The effects produced vary to some extent with the concentration.

In a 50% solution, cobaltous sulphate was formed below 70 milliamp./cm.^{2}. Immediately this *C.D.* was reached, however, the *P.D.* rose from 1·2 to 2·6 volts, and continued to oscillate regularly and rapidly (about one wave per second) between these two values, oxygen being evolved at the high potential. This periodicity was observed over a wide range, but above a *C.D.* of 250 milliamp./cm.^{2} the cobalt remained permanently in the passive state, oxygen being evolved continuously. The cobalt continued to dissolve when in the passive state, but formed a dark green solution of cobaltic sulphate. The surface of the metal appeared black throughout. The green colour did not appear in solutions weaker than this.

In 40% sulphuric acid, periodic passivity appeared at a *C.D.* of 105 milliamp./cm.^{2}, the *P.D.* oscillating between 1·1 and 2·8 volts in periods of 30 seconds' duration. In this system, it appeared that increase of *C.D.* *increased* the frequency—the reverse of what has been observed in all other systems. In solutions of concentration 30% and less, the effects were similar, except that a higher critical *C.D.* was required with increasing dilution and the periods were slower. 20 and 15% Solutions were best for observing changes in the state of the electrode, which correspond exactly with those recorded for iron. At the end of each passive period, during which the cobalt was lustrous, oxygen evolution ceased and the metal became dull; immediately before the next passive period a dark

grey film travelled up the anode and peeled off as the oxygen evolution began afresh.

Experiments in Other Solutions.—In hydrochloric acid (from 20 to 0·05%), nitric acid (100 to 0·5%), ammonium sulphate (10 to 1%), and sodium sulphate (10 to 2%) a cobalt anode did not become passive; on the other hand, in sodium hydroxide (8%) and potassium cyanide (20%) it became passive immediately and remained so after the circuit had been broken.

Nickel Anode.

Experiments in Sulphuric Acid Solutions.—The behaviour of nickel was similar to that of iron and cobalt. In 100 and 80% solutions, the *P.D.* soon rose to a high value, due to the formation of difficultly soluble nickel sulphate. Periodic passivity was observed in 60, 40, 30, 20, 10, and 5% solutions. The effect was less striking than in the foregoing instances, however, the amplitude being generally of the order of 0·2 volt.

As in the previous cases, oxygen was evolved during the passive periods and a dark film travelled up the metal immediately prior to its becoming passive.

Although the periods can be produced in the direct way by cautiously raising the *C.D.*, they are more easily started in the case of nickel by rendering the metal passive and then lowering the *P.D.* slightly. Thus in 5% sulphuric acid a nickel anode became passive at a *C.D.* of 102 milliamp./cm.^{2}, the *P.D.* rising from 1·4 to 2·9 volts. On lowering the *C.D.* to 70 milliamp./cm.^{2}, continuous oscillations between 2·3 and 2·5 volts followed at intervals of 5 seconds.

Experiments in Other Solutions.—In nitric acid (100, 75%), nickel did not appear to become passive, although it did so in more dilute solutions (25, 20, 10, and 5%). Periodicity was not observed in these solutions, however. In solutions of hydrochloric acid (30, 15, 5, 2, 0·5, and 0·1%) and of ammonium chloride (5, 2, 1, and 0·5%), the anode remained active at all current densities. Solutions of caustic soda (8%) and potassium cyanide (20, 10, 5, and 2·5%) caused passivity immediately, and ammonium sulphate (10, 5, and 2%) produced the passive state very readily. Periodic phenomena were not encountered in these systems.

Aluminium Anode.

Experiments in Nitric Acid Solutions.—Aluminium was used as an anode in 100% nitric acid at 30°. The metal dissolved continuously at low *C.D.*'s, but at 50 milliamp./cm.^{2} the *P.D.* oscillated regularly between 1·2 volts and 14·0 volts in periods of 20 seconds.

Slow evolution of gas occurred during these periods, but the surface of the electrode appeared to be unchanged. If, however, a very thin oxide film had formed periodically, it would probably have escaped observation, being transparent. Aluminium was not rendered passive in 80% nitric acid.

Experiments in Caustic Soda Solutions.—In an 8% solution, an anode of aluminium dissolved smoothly at moderate *C.D.*'s, hydrogen being evolved simultaneously when the current was sufficiently low. Hydrogen evolution ceased at about 60 milliamp./cm.^{2}. At 70 milliamp./cm.^{2}, a brass-coloured film appeared on the anode, and at 75 milliamp./cm.^{2} the *P.D.* oscillated in regular periods of 25 seconds between 1·65 and 2·0 volts, and a few bubbles, presumably of oxygen, were evolved. Above 110 milliamp./cm.^{2}, the *P.D.* remained constant. When a very small anode was employed, giving a high *C.D.* (roughly 10,000 milliamp./cm.^{2}), vigorous evolution of oxygen occurred and the metal remained bright. Periodic phenomena were observed also in 4% caustic soda.

Experiments in Other Solutions.—Solutions of hydrochloric, sulphuric, and orthophosphoric acids, sodium carbonate, and ammonium chloride were unsuitable for the production of periods.

The Conditions for Periodicity.

From the examination of a large number of periodic anodic reactions (Hedges, *loc. cit.*) it appears that when an anode can exist in one of two states, *e.g.*, with or without a film, then there exists a range of conditions (sometimes very narrow) in which the electrode is given more or less equal opportunities of being in either state, and the result is that it passes alternately from one to the other. The apparent truth of this generalisation has been demonstrated both in the case of anodes undergoing dissolution and in the case of film formation by deposition at an unattackable anode.

The experiments now described tend to show that periodic passivity is simply a special case, for it seems that periodicity ensues wherever the anode is given simultaneous opportunities of existing in the active or passive state. In order to test this point further, special experiments were devised in which a passivated anode was progressively activated, the idea being that at some stage, when activity and passivity were almost equally probable, the system would alternate continuously between the two states.

The progressive activation was effected in three ways: (*a*) By raising the temperature of the system, (*b*) by dilution of the reagent, (*c*) by addition of some agent favouring the active state.

(a) *Raising the temperature.* The system aluminium–100% nitric acid was used. At 20°, passivity readily set in and was

permanent. At 30°, the periods which have been described were produced. At 40°, the system still alternated between the two states, but very rapidly, the amplitude being only from 1·0 to 7·0 volts. At 60°, the aluminium remained active.

(b) *Dilution of the reagent.* The same system was taken and 0·5 c.c. of water was added to the nitric acid at 20°. Still the passivity was permanent when it developed. Further small additions of water were made until 2 c.c. had been added; oscillations between 1·7 and 13·4 volts with a 30-second period were then produced. An excess of water caused the aluminium to become

FIG. 1.

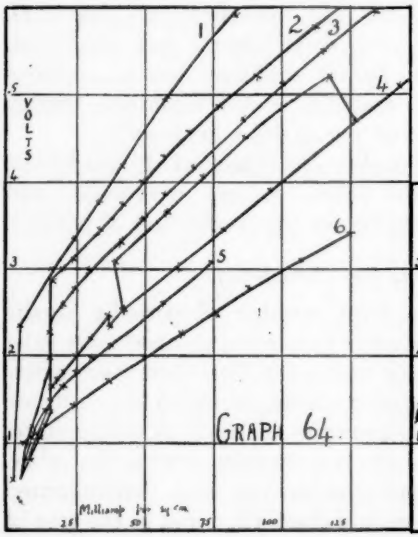
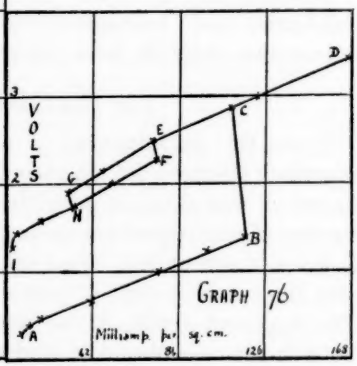


FIG 2.



completely active. In the experiments at 20°, a gelatinous, white, transparent film peeled off the anode; in one case, the solution was allowed to become warm and this film apparently dissolved in the acid at the higher temperature.

(c) *Addition of an agent favouring activity.* A nickel anode immediately becomes passive in 5% ammonium sulphate solution, as shown by the steep portion of Curve 1 (Fig. 1) where potential is plotted against current density; on the other hand it remains active in 5% ammonium chloride solution (Curve 6, Fig. 1). The behaviour of a nickel anode was examined in ammonium sulphate solutions containing progressively increasing quantities of ammonium chloride, in the expectation that a state would be reached at which the activating and passivating influences (whatever they

may be) balance each other, so that the electrode would alternate continually from one state to the other.

The results were as expected and are shown in Curves 2, 3, 4, and 5 (Fig. 1). The effect of adding 0·1% of ammonium chloride to the 5% ammonium sulphate is depicted by Curve 2, which shows that passivation occurs, but there is a shift in the direction of the active state. Addition of 0·2% of ammonium chloride is represented by Curve 3. Here the degree of passivation is still less. In the presence of 0·5% of ammonium chloride (Curve 4), passivation occurs to a smaller extent, but at a *C.D.* of 38 milliamp./cm.^{2} the nickel becomes active once more. Between this value and 125 milliamp./cm.^{2}, the anode alternates regularly between the active and passive states in periods of 5—10 seconds with an amplitude having a mean value of 0·6 volt. These limits of periodicity are represented in the graph by the quadrilateral. At *C.D.*'s greater than 125 milliamp./cm.^{2}, the nickel became permanently active. An equally good region of periodicity (not shown) was found when the solution contained 0·3% of ammonium chloride. The solution containing 1·0% of ammonium chloride is beyond the region of periodicity, the nickel remaining active throughout (Curve 5).

The table below records the values of *P.D.* for a given *C.D.* of 50 milliamp./cm.^{2} with progressive increase in the amount of ammonium chloride. It illustrates the region of periodicity lying on the border-line between two states.

		% NH_4Cl added to 5%$(NH_4)_2SO_4$.					
Soln.	5%$(NH_4)_2SO_4$	0·1%	0·2%	0·3%	0·5%	1·0%	5%NH_4Cl
P.D.	4·6	4·0	3·65	3·4 $\rightleftharpoons$ 2·8	3·4 $\rightleftharpoons$ 2·8	2·5	2·05

Periodicity and Passivity.

It has been shown (Hedges, *loc. cit.*) that the limits of periodicity at the anode are defined by exactly the same conditions for film formation as for what is regarded as passivity. It may be concluded either that passivity is a special case of film formation or that a region of periodicity may be a feature of several systems capable of different types of change of state. There is nothing novel in the first suggestion, but the evidence in its favour cannot be regarded as conclusive.

The analogy between the experiments now described and those conducted with other metals is illustrated in Fig. 2. This is a current density–potential curve for a nickel anode in 5% sulphuric acid and should be compared with Graph 50 (this vol., p. 2581), which is a similar curve for a zinc anode in caustic soda. The line *AB* represents the rise of *P.D.* with increasing *C.D.* until the point

represented by *B* is reached. At this critical *C.D.* the nickel becomes passive (or the zinc becomes enveloped in a film) and the *P.D.* rises to *C*, oxygen being evolved. Further increase in *C.D.* causes the *P.D.* to rise along the line *CD*. When the current is reduced, the *P.D.* retraces the same path to *C*, but continues as far as *E*. If the current density is reduced to those represented between *G* and *E*, the *P.D.* oscillates continuously between two values defined by the area *EGHF*, oxygen being evolved intermittently.

It is true that the nickel dissolves extremely slowly when passive, whereas the zinc in a similar state dissolves relatively rapidly, but that seems to be only a matter of degree—a change in the ratio of current employed in liberating oxygen to the current used in forming ions of the metal—which varies from metal to metal in any case.

On the other hand, the fact is now recorded for the first time (as far as the author is aware) that passivity is immediately preceded by the formation of a visible film, which disappears at the moment the electrode assumes the passive state. It will be recalled that in the experiments with a zinc anode in concentrated caustic soda solutions the film was flung from the metal each time oxygen was evolved, and it formed over the metal during the periods of lower potential.

No useful purpose would be served by drawing conclusions from these comparatively few experiments concerning a subject which has been controversial for almost a century, but it is hoped that the study of this type of periodicity may lead to a better understanding of the nature of passivity.

Summary.

Periodicity has been observed in the passivity of an iron anode in sulphuric, nitric, and phosphoric acids, a cobalt anode in sulphuric acid, a nickel anode in sulphuric acid, and an aluminium anode in nitric acid and in caustic soda. In each case, the effect is produced by so arranging conditions of concentration, current density, temperature, etc., that the electrode has approximately equal chances of being in the active or in the passive state. Under such conditions, the electrode oscillates regularly between the two states. Periodic phenomena may also be produced by electrolysis in a solution containing a mixture of passivating ions and activating ions, *e.g.*, by adding ammonium chloride to an ammonium sulphate solution in which a nickel anode has been made passive. The periodic passivity phenomenon does not seem to differ in any respect from the periodic film formation at other metallic anodes. Immediately before passivation of the anode a visible film forms over the

metal, but this disappears at the commencement of oxygen evolution. The bearing of these observations on the nature of passivity is considered.

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CCCLXXXV.—*Studies of Electrolytic Polarisation. Part IV. The Electro-deposition Potentials of Iron, Cobalt, and Nickel.*

BY SAMUEL GLASSTONE.

IT is well known that, in order to cause the electro-deposition of the metals of the iron group from aqueous solutions of even their simple salts, it is necessary to apply a cathodic potential which is considerably more negative than the theoretically reversible potential in the same solution; there is thus an "overvoltage" or retardation of metallic deposition. In every case, owing to the low overvoltage of hydrogen at these metal surfaces, the evolution of this gas accompanies the electro-deposition of the metal, and consequently hydrogen gas or hydrogen ions have been commonly regarded as the chief factor retarding the deposition of metal. In general, we may say that the deposition of a bivalent metal at the cathode involves the process

$$\underset{\text{(Ions in soln.)}}{M^{\cdot\cdot}} + 2\ominus \longrightarrow \underset{\text{(Atoms deposited.)}}{M}.$$

If this process occurs rapidly there will be no accumulation of ions in the vicinity of the cathode and the metal will be deposited at its normal reversible potential; on the other hand, if this process is retarded, deposition will not occur at this potential and the electrode will become polarised. When the potential is made more negative, the increased electron concentration will enable the above process to take place sufficiently rapidly for metallic atoms to be deposited. According to Foerster (*Z. Elektrochem.*, 1916, **22**, 85), hydrogen gas acts as a negative catalyst for the above process in the case of iron, cobalt, and nickel, and consequently the simultaneous deposition of hydrogen retards the deposition of metal. It should be pointed out that the deposition process which was considered to be retarded is a heterogeneous one, since the ions

are in solution and the atoms are deposited on the solid electrode; Smits ("The Theory of Allotropy," 1922, pp. 132, 334; *Trans. Faraday Soc.*, 1924, **19**, 772), however, considers that heterogeneous equilibrium is always reached rapidly and that ions and electrons are deposited on the cathode as fast as they are brought up to it. The combination between ions and electrons is then supposed to occur in the solid electrode and is consequently a homogeneous process; if this process does not occur rapidly, then ions and electrons will accumulate until an increased negative potential results in a greater electron concentration and a consequent removal of ions to form undissociated atoms. Smits considers that hydrogen gas is a negative catalyst for this process which occurs in the solid electrode. Kohlschütter (see *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 229, for summary), on the other hand, attributes an entirely different rôle to the hydrogen which is liberated with the metal; a film of compressed gas is said to be present at the cathode, and it is considered that metallic atoms are deposited in this medium, which has considerable viscosity. The film of hydrogen behaves like an adsorption film of colloid in metal deposition and prevents the aggregation of small, metallic crystals. The metal is thus deposited in a highly dispersed form with a high free energy, and therefore an excess negative potential is required for its deposition; this form of metal, however, is in a state of strain and so there will be some tendency, opposed by the gas film, for it to change into a more stable form and thus give rise to the well-known contraction and peeling effects observed in the deposition of the iron-group metals. Kohlschütter (*loc. cit.*) deduces that with decreasing hydrogen-ion concentration of the electrolyte the polarisation should first increase, pass through a maximum, and then decrease; the argument is, however, open to objection. It is considered, too, that the contraction of the metallic deposit should vary in the same manner with varying hydrogen-ion concentration of the electrolyte; but Alvierti (*Atti R. Accad. Lincei*, 1920, **29**, 453) states that the contraction of a nickel deposit is decreased by simultaneous evolution of hydrogen in proportion to the amount evolved, and this will obviously be greater in solutions of greater hydrogen-ion concentration. Frölich and Clark (*Z. Elektrochem.*, 1925, **31**, 649) have shown that there is a similarity between the overvoltage of metal deposition and the hydrogen overvoltage at the cathodes of these metals; for example, iron, cobalt, and nickel have large metal deposition overvoltages but small hydrogen overvoltages, but with mercury and lead the conditions are reversed. Adopting the "hydride" theory, these authors attribute the overvoltage of metal deposition to the form-

ation of stable hydrides in the case of the low-overvoltage metals; the deposition of metal does not occur until the hydride has accumulated to a sufficient extent to decompose rapidly and so polarisation results. Le Blanc (*Trans. Faraday Soc.*, 1914, **9**, 251) has put forward a theory in which hydrogen appears to play no part; it is considered that the dehydration of the ions in solution must occur before the unhydrated ions can take up electrons and then be deposited. If the dehydration process occurs slowly, polarisation will result and a higher cathodic potential will be required in order to cause deposition of metal; this would be similar to the polarisation which is observed in the electrolysis of cuprocyanide solutions owing to the slowness of the process $Cu(CN)_2' \longrightarrow Cu^{\cdot} + 2CN'$ (Le Blanc and Schick, *Z. physikal. Chem.*, 1903, **46**, 213). It is doubtful whether hydrogen gas could influence the speed of the dehydration, although it is possible that certain ions, competing with the metallic ion for water molecules, might influence the degree of hydration and the rate of dehydration. This theory was accepted by Newbery (J., 1917, **111**, 470), and Isgarishev and Berkmann (*Z. Elektrochem.*, 1922, **28**, 40) consider that they have obtained evidence in favour of the dehydration hypothesis.

An examination of these theories shows that it is essential to know exactly how the overvoltage of metal deposition varies with the hydrogen-ion concentration of the electrolyte; some work in this connexion has been done by Schweitzer (*ibid.*, 1909, **15**, 602) and by Schildbach (*ibid.*, 1910, **16**, 967), but the summary given by Foerster (*loc. cit.*) shows the difficulty of interpreting the results. It appeared to the present author that the use of a series of buffer solutions of known hydrogen-ion concentrations and the application of his extrapolation method for measuring the potentials of polarised electrodes (J., 1924, **125**, 250, 2414) might throw further light on the subject of the electro-deposition of the iron-group metals.

Experimental.

Electrolytic Solutions.—The requisite amount of nickel, iron, or cobalt salt was added to a buffer solution—usually one of Walpole's (J., 1914, **105**, 2501)—and the hydrogen-ion concentration of the solution roughly determined by means of indicators. In some cases potassium sulphate was added in order to increase the conductance of the solutions.

Electrodes.—The cathodes were sheets of copper foil, generally of about 7·5 sq. cm. exposed area, on which the metal under investigation was deposited by electrolysis; the anode consisted always of a short piece of platinum wire. Whenever iron or chloride solu-

tions were being electrolysed, or when it was desired to exclude oxygen from the solution, the cathode was placed inside a porous pot and the anode in the surrounding liquid.

Materials.—The ferrous sulphate was of A.R. quality and the nickel and cobalt sulphates were good commercial specimens supplied by the British Drug Houses, Ltd. Some experiments were made with a special sample of nickel sulphate which was free from iron and cobalt, but the results did not appear to differ from those given by the less pure material. The other salts used were the purest obtainable commercially, and, where possible, of A.R. quality.

Measurement of Potential.—The current passing between the electrodes was increased by stages and was held constant for 1 minute before the potential of the electrode was measured by the commutator-extrapolation method, using the commutator described in previous work (J., 1923, **123**, 2926). The reference electrode was in every case a calomel electrode in a saturated solution of potassium chloride; no allowance was made for diffusion potential.

Deposition of Nickel.—Table I gives the cathodic potentials, on the H_2(1 atm.)|N-H$^{\cdot}$ = 0 scale, of a nickel electrode at various *C.D.*'s in various acetate buffer solutions containing N-nickel sulphate; in one case, a $N/50$-sulphuric acid solution was used instead of a buffer mixture. All experiments in this series were carried out at room temperature (roughly 15°).

TABLE I.

C.D. (amps. × 10^{-4}/cm.^{2}).	Cathode potentials in N-$NiSO_4$.				
	$N/50$-H_2SO_4.	p_H 2·8.	p_H 4·0.	p_H 5·0.	p_H 6·0.
0·14	−0·14	−0·18	−0·21	−0·25	−0·26
0·28	−0·18	−0·22	−0·24	−0·30	−0·31
0·42	−0·21	−0·29	−0·28	−0·35	−0·39
0·56	−0·24	−0·34	−0·34	−0·39	−0·45
0·84	−0·30	−0·40	−0·39	−0·46	−0·50
1·40	−0·37	−0·45	−0·45	−0·54	−0·57
2·80	−0·43	−0·51	−0·52	−0·58	−0·58
4·20	−0·47	−0·57	−0·57	−0·60	−0·60
5·60	−0·52	−0·58	−0·59	−0·61	−0·62
8·40	−0·57	−0·59	−0·60	−0·62	−0·64
12·0	−0·59	−0·61	−0·61	−0·63	−0·66
20·0	−0·60	−0·62	−0·62	−0·64	
40·0	−0·61	−0·64	−0·64	−0·65	
80·0	−0·62	−0·65	−0·65	−0·66	

For purposes of comparison, the cathodic potential of a polarised nickel electrode in the acetate buffer solutions of p_H 5·0 and 6·0 alone (*i.e.*, no nickel salt being present) at various *C.D.*'s is given in Table II.

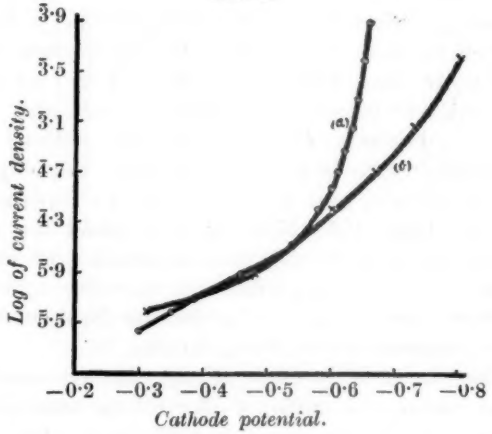
TABLE II.

Cathode Potentials.

C.D. (amps. × 10^{-4}/cm.^{2})	0·28	0·56	0·84	1·40
p_H 5·0	−0·19	−0·39	−0·48	−0·54
p_H 6·0	−0·36	−0·44	−0·54	−0·72
C.D. (amps. × 10^{-4}/cm.^{2})	2·80	5·60	12·0	40·0
p_H 5·0	−0·60	−0·67	−0·73	−0·80
p_H 6·0	−0·83	−0·92	−0·97	−1·00

An examination of Table I shows that in each case the cathode potential rises fairly rapidly, with increasing *C.D.*, until a value of − 0·57 volt is reached, after which it only changes very slightly. By comparing the results given in Tables I and II and also the

FIG. 1.



log *C.D.*–potential curves in Fig. 1 for a solution of p_H 5·0, (*a*) containing *N*-nickel sulphate and (*b*) in the absence of nickel salt, it is seen that there is a distinct break at the potential of − 0·57 volt in the solutions containing nickel sulphate, and sometimes a slight break at the potential at which hydrogen is first evolved * (− 0·41 volt in solution of p_H 5·0). The difference in the two curves (Fig. 1) can only be due to the presence of nickel ions in one of the solutions, and it was always observed that nickel was deposited on the cathode when the potential exceeded that at the break-point. It seems probable, therefore, that the break at the potential of − 0·57 volt is due to the commencement of the deposition of nickel at 15°; this initial deposition potential is independent of the hydrogen-ion concentration of the electrolytic solution. By using a polished

* The minimum (or bubble) overvoltage of hydrogen at a nickel cathode was 0·12 volt (approx.) in all the solutions examined, at room temperature.

copper cathode, the lowest *C.D.* at which nickel was deposited from any solution could be readily determined by observation of the electrode surface after being used for a short time at each of a number of gradually increasing *C.D.*'s; the potential at the lowest *C.D.* necessary for nickel deposition was always very near to — 0·57 volt. It is possible that this potential may have been affected by the formation of a nickel–copper alloy, but the coincidence of the minimum potential for metal deposition with the breaks in the *C.D.*–potential curves suggests very strongly that nickel commences to be deposited from a *N*-solution of its sulphate at a potential of — 0·57 volt at 15°, independently of the hydrogen-ion concentration. It will be observed that, as the hydrogen-ion concentration of the solution increases, the *C.D.* at which nickel deposition commences becomes higher; this is to be expected, since, with increasing concentrations of hydrogen ions, a larger current can be carried by these ions without having recourse to the nickel ions. It is quite clear that the practice hitherto adopted of comparing the cathode potentials in different solutions at the same *C.D.* (see, *e.g.*, Foerster, *loc. cit.*) may not indicate the general behaviour of the electrode in these solutions; the only satisfactory method of comparison, as in the investigation of hydrogen evolution (Glasstone, J., 1924, **125**, 2414), is to consider the potentials at which a new process—in this case deposition of metal—is just commencing. The trustworthiness of the above results for the minimum deposition potential of nickel has been confirmed by the following experiments with other solutions.

In order to determine the effect, if any, of anions on the deposition potential of nickel, a number of electrolytic solutions were used which contained only one anion in addition to the hydroxyl ion; in one case, nickel acetate was dissolved in the acetate buffer solution, whilst other solutions consisted of nickel sulphate only, nickel sulphate in *N*/10-sulphuric acid, nickel chloride in *N*/50-hydrochloric acid, nickel nitrate in *N*/50-nitric acid, saturated nickel ammonium sulphate, and saturated nickel potassium sulphate. Other solutions were the same as those used in the first part of this work, with the addition of ammonium persulphate, hydrogen peroxide, or gelatin. In every case, deposition of nickel commenced at a potential of — 0·57 volt at 15° from a *N*-solution of a nickel salt. The *C.D.* at which deposition commenced varied somewhat in the different solutions and was much higher in those containing oxidising agents, but the potential was always constant within 0·01 volt. The use of a wire cathode did not affect the results (compare Küster, *Z. Elektrochem.*, 1901, **7**, 688), neither did the complete elimination of gaseous oxygen by working in an atmo-

sphere of hydrogen. By altering the concentration of nickel salt in the solution to $N/100$, the deposition potential became 0·06 volt more negative; this agrees with the change in the concentration of bivalent nickel ions.

A series of experiments was performed at 95°, using the same nickel sulphate and acetate buffer solutions; the results are given in Table III. The p_H values are only approximate owing to the change in temperature. The cathode potentials of a nickel electrode in an acetate buffer solution only, of p_H 6, are given in col. 6 for purposes of comparison.

TABLE III.

Cathode potentials in N-$NiSO_4$ at 95°.

C.D. (amps. × 10^{-4}/cm.^{2}).	p_H 2·8.	p_H 4.	p_H 5.	p_H 6.	p_H 6 (no Ni).
2·8	−0·16	−0·19	−0·23	−0·28	−0·25
4·2	−0·17	−0·21	−0·24	−0·29	−0·29
5·6	−0·18	−0·23	−0·25	−0·30	−0·31
8·4	−0·21	−0·26	−0·26	−0·30	−0·34
12·0	−0·23	−0·28	−0·27	−0·30	−0·37
20·0	−0·26	−0·29	−0·29	−0·30	−0·41
40·0	−0·29	−0·30	−0·30	−0·31	−0·44
80·0	−0·30	−0·31	−0·31	−0·31	−0·45
160·0	−0·31	−0·31	−0·31	−0·31	−0·47

These results indicate that the change in direction of the *C.D.*–potential curves for nickel solutions occurs at about − 0·29 volt; this may be regarded as the deposition potential of nickel from a N-solution of its simple salts at a temperature of 95°. Observations with a polished copper cathode have established the fact that no nickel is deposited at this temperature until the potential reaches − 0·29 volt. Experiments with solutions of nickel chloride and acetate led to the same conclusion.

Measurements have also been made at 55°, at which temperature nickel commences to be deposited at a potential of − 0·43 volt; this value is independent of the hydrogen-ion concentration of the solution. Table IV summarises the results for different temperatures.

TABLE IV.

Deposition potential of nickel from N-solutions.

Temperature	15°	55°	95°
Potential	−0·57	−0·43	−0·29
Overvoltage	0·33	0·19	0·05

The overvoltage values have been obtained by taking − 0·24 volt as the reversible potential of the Ni|N-$NiSO_4$ electrode (*Abh. Deut. Bunsengesellschaft*, No. 5, 1911), and neglecting its small temperature coefficient. The temperature coefficient of overvoltage of nickel deposition is thus − 0·0035 volt/degree over the range investigated.

Deposition of Iron.—Table V contains the results of a series of measurements with N-ferrous sulphate in acetate buffer solutions of varying p_H, and in one case in $N/50$-sulphuric acid, at 15°.

TABLE V.

C.D. (amps. $\times 10^{-4}$/cm.^{2}).	Cathode potentials in N-$FeSO_4$.			
	$N/50$-H_2SO_4.	p_H 2·8.	p_H 4·0.	p_H 5·0.
0·14	−0·46	−0·47	−0·47	−0·47
4·2	−0·46	−0·49	−0·49	−0·53
8·4	−0·46	−0·52	−0·50	−0·58
20·0	−0·48	−0·57	−0·56	−0·60
40·0	−0·53	−0·68	−0·68	−0·68
80·0	−0·68	−0·70	−0·69	−0·70
160·0	−0·70	−0·71	−0·71	−0·71

These results show that in every case the cathode potential increases at first slowly, then jumps to the value − 0·68 volt, after which the increase, with increasing *C.D.*, is comparatively slow. This potential, at which the *C.D.*–potential curve changes its direction, has been found, by observations with a polished copper cathode, to be that at which electro-deposition of iron commences from a N-solution of its simple salts. Experiments have been made with ferrous ammonium sulphate solutions, both in the presence and the absence of free sulphuric acid, and with ferrous chloride in $N/50$-hydrochloric acid and in acetate buffer solutions; in every case, the deposition potential of iron at 15° is − 0·68 ± 0·01 volt.

Measurements of the initial deposition potential of iron have also been made at other temperatures and the results are summarised in Table VI.

TABLE VI.

Deposition potential of iron from N-solutions.

Temperature	15°	36°	55°	70°	90°
Potential	−0·68	−0·55	−0·49	−0·46	−0·46
Overvoltage	0·22	0·09	0·03	Nil.	Nil.

The reversible potential of iron in a N-solution of a simple ferrous salt is probably − 0·46 volt (Hampton, *J. Physical Chem.*, 1926, **30**, 980), and so it appears that at temperatures above about 70° iron may be deposited almost reversibly.

Deposition of Cobalt.—Measurements with N-solutions of cobalt salts have been made as with nickel and iron; the results are summarised in Tables VII and VIII. In each case, independently of the hydrogen-ion concentration, there is a break in the variation of potential with *C.D.* at − 0·56 volt; this is the potential at which deposition of cobalt commences. Experiments with cobalt chloride in hydrochloric acid solution, with the nitrate in nitric acid, and with the acetate in acetate buffer solutions all gave a similar result.

TABLE VII.

C.D. (amps. × 10^{-4}/cm.^{2}).	Cathode potentials in N-$CoSO_4$ at 15°. $N/10$-H_2SO_4.	p_H 2·8.	p_H 4·0.	p_H 5·0.	p_H 6·0.
0·14	−0·19	−0·17	−0·19	−0·22	−0·24
0·56	−0·22	−0·22	−0·34	−0·39	−0·44
1·4	−0·31	−0·42	−0·49	−0·56	−0·56
2·8	−0·36	−0·46	−0·56	−0·57	−0·57
5·6	−0·42	−0·51	−0·57	−0·59	−0·59
12·0	−0·49	−0·56	−0·59	−0·61	−0·61
40·0	−0·56	−0·57	−0·61	−0·62	−0·63
80·0	−0·57	−0·59	−0·62	−0·63	−0·64
160·0	−0·58	−0·60	−0·63	−0·64	−0·65

TABLE VIII.

Deposition potential of cobalt from N-solutions.

Temperature	15°	55°	95°
Potential	−0·56	−0·46	−0·36
Overvoltage	0·25	0·15	0·05

The reversible potential of the electrode Co|N-$CoSO_4$ has been taken as − 0·31 volt (*Abh. Deut. Bunsengesellschaft*, No. 5, 1911), and the temperature coefficient has been neglected. The temperature coefficient of overvoltage of cobalt deposition is thus − 0·0025 volt/degree.

Discussion of Results.

The fact that the potentials at which the metals iron, nickel, and cobalt begin to be deposited are independent of the hydrogen-ion concentration of the electrolyte—within the range of p_H investigated, *i.e.*, roughly 2 to 6—throws doubt on some of the theories which have been suggested to account for the retardation of the deposition of these metals. In a N-solution of a simple nickel salt, the reversible potential is about − 0·24 volt; at this potential, the hydrogen pressure in the electrode is roughly equivalent to 10^4 atms. in a solution of p_H 2, and to 10^{-4} atm. in a solution of p_H 6. According to the views of Foerster (*loc. cit.*), Smits (*loc. cit.*), and Kohlschütter (*loc. cit.*), we should expect that the overvoltage of metal deposition would be affected by the concentration of hydrogen gas at the electrode, yet actually this does not appear to be so. The deposition potential, too, is probably not so much affected by the structure of the deposit as Kohlschütter imagines, because the presence of a depolariser (*e.g.*, hydrogen peroxide) causes scarcely any change in the deposition potential although it is said to influence the contraction of the deposit. If we accept the "hydride" theory of Frölich and Clark (*loc. cit.*), we also obtain conflicting conclusions. Since the minimum overvoltage of any metal is almost independent of the hydrogen-ion concentration of

the electrolyte (J., 1924, **125**, 2414, **2646**; and unpublished measurements with nickel, copper, tin, and cadmium), it may be inferred that the "hydride" has a fairly definite composition; the constancy of the deposition potential, however, would suggest that in the deposition of metal the composition of the "hydride" varies with the hydrogen-ion concentration of the solution. From Le Blanc's theory, we should expect not so much a large overvoltage for the initial deposition potential of the metal as a rapidly increasing polarisation with increasing *C.D.* and increasing rate of metal deposition. The *C.D.*–cathode potential curves should be of the type obtained by Spitzer (*Z. Elektrochem.*, 1905, **11**, 345) during the electrolysis of solutions of the complex cyanides of copper and zinc; the actual curves, however, are not at all of this type, for although an excess potential has to be applied in order to initiate deposition, yet the subsequent polarisation is very little more than that occurring during the deposition of mercury, lead, or copper from solutions of their simple salts. This serious objection to Le Blanc's theory probably applies also to the other reaction-velocity theories, for in every case we should expect the polarisation effect to increase rapidly with increasing rate of metal deposition.

As an alternative to the theories discussed above, the following tentative hypothesis is suggested. In the ions of iron, cobalt, and nickel, although the 3-quantum orbit of electrons is not completed, yet we know that there is a tendency for some additional electrons to go into a 4-quantum orbit. If when a nickel ion takes up two electrons at the cathode they both enter the 4-quantum orbit, then an atom with the electronic arrangement 2, 8, 16, 2 results; this metastable atom may have, like the zinc atom (2, 8, 18, 2), a strong tendency to lose its last two electrons, and so it would be a strongly electropositive metal having a deposition potential more negative than that of ordinary stable nickel, with a possible arrangement of 2, 8, 17, 1 * (compare Kramers and Holst, "The Atom and the Bohr Theory of Its Structure," 1923, p. 209). The metastable form would be transformed spontaneously, but at a definite rate, into ordinary nickel, and so the actual deposit would consist of a system of two forms of nickel; this system would be deposited at a potential lying between the reversible potential of ordinary nickel and that of the more electropositive unstable form, and thus an excess potential over that of ordinary nickel would be required before deposition could commence. There appears to be no reason why the composition of the deposited metal should vary appreciably with the *C.D.*, and so there should be no large polarisation effects

* Russell (*Nature*, 1925, **115**, 455) has suggested that *ordinary* nickel has the arrangement 2, 8, 16, 2, whilst 2, 8, 17, 1 is that of *passive* nickel.

as the rate of metal deposition is increased; this is in agreement with the observed facts. The composition of the deposit should depend only on the rate of transformation of the unstable to the stable form of metal, and this will depend almost solely on the temperature; at each temperature, therefore, the deposit will have a definite composition and consequently a definite deposition potential dependent only on the concentration of metal ions in the electrolyte. At higher temperatures, the rate of transformation into the stable form will be increased and so the deposit will contain more ordinary nickel and the deposition potential will approach more and more the reversible nickel potential. These suggestions apply equally well to the deposition of iron and cobalt. The contraction observed in the electro-deposits of these three metals may be attributed partly to the change from unstable to stable form which occurs in the deposit subsequent to deposition; it is probable, however, that the simultaneous evolution of hydrogen has some influence.

Summary.

(1) By the use of the commutator-extrapolation method of measuring the potentials of polarised electrodes, the initial deposition potentials of iron, cobalt, and nickel have been measured at a number of temperatures in a series of solutions of varying hydrogen-ion concentration.

(2) The deposition potential has in each case been found to be independent of the hydrogen-ion concentration of the solution and of the anions present. Depolarisers, too, do not appear to affect the results.

(3) The theories which have been advanced to account for the retardation of the deposition of the iron-group metals are examined and found not to be in agreement with the observed facts.

(4) An alternative theory is suggested according to which the metals are primarily deposited in an unstable form with a different electronic arrangement from that of the ordinary form.

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CCCLXXXVI.—*Studies of Electrolytic Polarisation. Part V. The Electro-deposition Potentials of Alloys of Iron, Cobalt, and Nickel.*

By SAMUEL GLASSTONE.

As a consequence of experiments on the electro-deposition potentials of iron, cobalt, and nickel (preceding paper), it was decided to extend the observations to the initial potentials at which alloys of

these metals are deposited from mixed solutions of their salts. Some general observations have been made by Küster (*Z. Elektrochem.*, 1901, **7**, 688) and by the author (*Trans. Faraday Soc.*, 1924, **19**, 574), but the results are not trustworthy, since they include the errors inherent in the direct method of measuring polarisation potentials, and, moreover, no attempt was made to regulate the hydrogen-ion concentration of the electrolyte. In the work now described, acetate buffer solutions were used in order to maintain a fairly definite hydrogen-ion concentration, and the polarisation potentials were measured by the author's commutator–extrapolation method.

Experimental.

The materials and procedure were as described in the preceding paper, Walpole's acetate–acetic acid solutions again being used as the basis for almost all of the electrolytic baths. The solutions contained varying amounts of the sulphates of two or three of the iron-group metals, the total concentration of these metals being one g.-equiv. per litre. The cathodes were of copper covered with a complete layer of alloy deposited at fairly low *C.D.* from the solution under examination; the exposed part was generally 7·5 sq. cm. in area. When the solutions contained iron salts, the anode and cathode compartments were separated.

Nickel–Iron Alloys.—The potentials recorded in Table I were obtained with a solution containing equivalent amounts of iron and nickel in solutions of varying hydrogen-ion concentration at 15°. (Throughout this paper current densities are expressed in terms of amps. $\times 10^{-4}$ per sq. cm.)

Table I.

Cathode potentials in 1Fe : 1Ni solution.

C.D.	$N/10$-H_2SO_4.	p_H 2·8.	p_H 4·0.	p_H 5·0.
0·42	−0·33	−0·36	−0·38	−0·44
1·40	−0·36	−0·38	−0·46	−0·52
2·80	−0·39	−0·41	−0·53	−0·55
5·60	−0·43	−0·50	−0·56	−0·59
8·40	−0·48	−0·55	−0·58	−0·66 *
12·0	−0·52	−0·58	−0·67 *	−0·68
20·0	−0·54	−0·65 *	−0·69	−0·70
40·0	−0·58	−0·67	−0·71	−0·71
80·0	−0·66 *	−0·69	−0·72	−0·72
160·0	−0·68	−0·71	−0·73	−0·73

* Break-point.

In each case, with increasing *C.D.* the potential increases at first slowly, then jumps suddenly to a value that is always very near to − 0·66 volt, after which it changes comparatively slightly. Observations with a polished copper cathode (see preceding paper)

indicate that the potential noted as "break-point" in Table I is that at which deposition of metal commences; this is in agreement with the results obtained in the deposition of the single metals. It appears, therefore, that from a solution containing equivalent amounts of nickel and iron an alloy commences to be deposited at a potential of — 0·66 volt independently of the hydrogen-ion concentration of the solution; the *C.D.* at which deposition commences will, of course, be lower the smaller the hydrogen-ion concentration of the solution.

The measurements were repeated with solutions containing other ratios of iron and nickel, and the results were of exactly the same type as those given in Table I. A summary is contained in Table II. The temperature was approximately 15° throughout.

TABLE II.

Solution : 1Fe : 9Ni.

	p_H 2·8.	p_H 4·0.	p_H 5·0.	p_H 6·0.
Initial deposition potential	−0·59	−0·60	−0·60	−0·59
Current density	8·4	8·4	5·6	4·2

Solution : 3Fe : 7Ni.

	p_H 2·8.	p_H 4·0.	p_H 5·0.
Initial deposition potential	−0·64	−0·63	−0·63
Current density	20·0	12·0	5·6

Solution : 7Fe : 3Ni.

	p_H 2·8.	p_H 4·0.	p_H 5·0.	$N/50$-H_2SO_4.
Initial deposition potential	−0·68	−0·68	−0·68	−0·67
Current density	40·0	20·0	8·4	40·0

The experiments were repeated at 55° and at 95° and the initial deposition potentials of the alloys from electrolytes of varying composition were determined. The results are summarised in Table III.

TABLE III.

Ratio Fe : Ni in solution.	Deposition potential at 15°.	55°.	95°.
Ni only.	−0·57	−0·43	−0·29
1 : 9	−0·595	−0·44	−0·29
3 : 7	−0·63	−0·45	−0·30
1 : 1	−0·66	−0·46	−0·31
7 : 3	−0·68	−0·49	−0·35
Fe only.	−0·68	−0·50	−0·46

TABLE IV.

Ratio Fe : Co in solution.	Deposition potential at 15°.	55°.	95°.
Co only.	−0·56	−0·46	−0·36
1 : 9	−0·60	−0·46	−0·36
3 : 7	−0·62	−0·46	−0·36
1 : 1	−0·64	−0·47	−0·38
7 : 3	−0·67	−0·49	−0·40
Fe only.	−0·68	−0·50	−0·46

Tables IV, V, and VI, respectively, give the deposition potentials found for alloys from solutions containing the sulphates of iron and cobalt, nickel and cobalt, and iron, cobalt, and nickel. Except in the last case, data are given for 15°, 55°, and 95°.

TABLE V.

Ratio Ni : Co in solution.	Deposition potential at 15°.	55°.	95°.
Ni only.	−0·57	−0·43	−0·29
3 : 1	−0·57	−0·44	−0·32
1 : 1	−0·57	−0·44	−0·32
1 : 3	−0·57	−0·45	−0·34
Co only.	−0·56	−0·46	−0·36

TABLE VI.

Ratio in solution. Fe	Co	Ni	Deposition potential at 15°.
1	4·5	4·5	−0·57
1	2	1	−0·58
1	1	2	−0·60
1	1	1	−0·63
2	1	1	−0·68

Discussion.

An examination of Table III shows that at 15° the deposition potential increases rapidly at first with increasing iron ratio in the electrolyte; thus, when only half of the dissolved salt is ferrous sulphate, the deposition potential (− 0·66) is very close to that of pure iron (− 0·68). If we adopt the view that the metal which is primarily deposited is a metastable form with an electronic arrangement which differs from that of the ordinary metal and subsequently changes into it (see preceding paper), then the results obtained in this work indicate that the rate of change of metastable to stable form is hindered by the simultaneous deposition of a small amount of iron. Thus the initial deposition occurs at a potential which is more negative than that at which pure nickel is deposited; since the former potential approaches that at which pure iron is deposited from a ferrous sulphate solution, it is probable that even the initial deposit will contain a fairly large proportion of this metal. If the *C.D.* is raised, the polarisation potential also rises, and so the amount of iron in the deposit will tend to increase; this increased proportion of iron will exert an additional retarding effect on the change of metastable to stable nickel, with the result that the deposition of nickel requires a still more negative potential. The deposit will thus tend to contain even less nickel, and so with increasing *C.D.* the proportion of iron should increase very rapidly. This increase is soon counteracted, since the deposit will contain a much larger proportion of iron than does the electrolyte, and the solution will become relatively richer in nickel ions in the vicinity of the electrode; thus an alloy somewhat poorer in iron will be deposited and eventually a point of balance will be reached at which the composition of the alloy remains constant even if the *C.D.* is increased. A further *large* increase of *C.D.*, especially in dilute solution, may result in an actual decrease in the proportion of iron in the deposited alloy owing to the impoverishment of the electrolyte. At higher temperatures, it is clear from the results that iron has very much less influence on the rate of the nickel transformation, since the deposition potentials are much nearer

those at which pure nickel can be deposited. We should thus expect the deposits from a given solution to contain much less iron than at ordinary temperatures (compare Kremann, *et al.*, *Monatsh.*, 1913, **34**, 1757; 1914, **35**, 731) and the increase of the proportion of iron with increasing *C.D.* to be much more gradual. When the amount of iron in the electrolyte is increased, the behaviour should approach more closely that found at ordinary temperatures. In order to test these predictions, a comprehensive series of investigations has been commenced on the variation of the composition of alloys deposited from solutions containing two of the iron-group metals at different concentrations and at a number of *C.D.*'s. An examination of Table I shows that at a given *C.D.* the potential may depend on the hydrogen-ion concentration of the solution, and hence the composition of the alloy may also depend on this. It is thus essential that the hydrogen-ion concentration of the electrolyte be kept as constant as possible during the course of the experiment in which the alloy is being deposited; failure to observe this precaution may account for the results of Toeppfer (*Diss.*, Breslau, 1899; *Z. Elektrochem.*, 1899, **6**, 342) and also for the apparent variation of the composition of the alloy with time found by Foerster ("Elektrochemie Wässeriger Lösungen," 1922, p. 376). The preliminary observations at ordinary temperatures which have been made so far in connexion with the deposition of nickel–iron alloys indicate that the initial deposit often contains relatively less iron than does the electrolyte, but the proportion increases at first rapidly with increasing *C.D.*, then more slowly, and finally reaches an almost constant value.

The results obtained in the deposition of iron–cobalt alloys (Table IV) are similar to those for the iron–nickel alloys. The retarding effect of iron on the change of metastable cobalt to the stable form appears to be less than in the case of nickel. We should expect, therefore, that the alloys would not be so rich in iron and that the increase of iron concentration in the deposit with increasing *C.D.* should be somewhat less rapid than is the case with nickel–iron alloys deposited under similar conditions. The experiments now in hand will give further information on these points.

The case of the nickel–cobalt alloys (Table V) is interesting but inconclusive: it indicates the necessity for an investigation, which is being undertaken, on the variation in composition of the alloys with changes in the conditions of deposition.

Table VI affords but little information regarding the iron–cobalt–nickel alloys; it appears, however, that the effect of iron in retarding the change of metastable to stable atoms is less in the presence

of a mixture of cobalt and nickel than in that of either of these metals alone.

It is considered very unlikely that cobalt or nickel can appreciably retard the conversion of metastable iron into the stable form; if this retardation were possible, then alloys rich in iron, but containing a small proportion of nickel or cobalt, should commence to be deposited only at potentials more negative than that at which pure iron may be deposited. This has, however, not been observed.

Summary.

(1) The initial deposition potentials of alloys of iron, nickel, and cobalt, in pairs or all together, from solutions of various metallic and hydrogen-ion concentrations have been measured at 15°, 55°, and 95°.

(2) The deposition potential varies with the ratio of the metals in solution and with the temperature, but is independent of the hydrogen-ion concentration.

(3) The results are discussed in the light of a theory previously proposed to account for the overvoltage of deposition of the iron-group metals. It appears that in the deposition of alloys of iron with nickel and with cobalt the concentration of iron in the alloy should increase at first rapidly with increasing current density and then reach an almost constant value.

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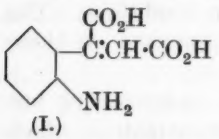
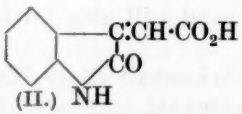
CCCLXXXVII.—*The Relative Stability of the Quinolone and Indolinone Rings.*

By JOHN ALFRED AESCHLIMANN.

Two lactams are derivable from β-carboxy-*o*-aminocinnamic acid (I), and when ring closure takes place on acidification of its alkaline solution either the indolinone (II) or the quinolone (III) will be produced according as the one or the other is the more stable.



(I.)



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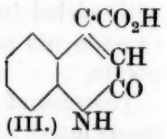
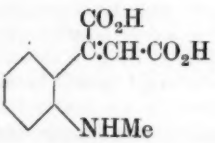


(III.)

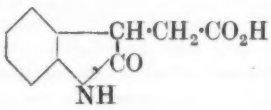
Koenigs and Nef (*Ber.*, 1879, **12**, 100) and Koenigs and Koerner (*Ber.*, 1883, **16**, 2152) oxidised quinoline-4-carboxylic acid by fusion with potash to an acid to which the structure (III) was assigned on account of the production of carbostyril by distillation of the silver salt. This evidence, however, is not conclusive in

view of the high temperature involved. The same acid was obtained by Camps (*Arch. Pharm.*, 1899, **237**, 687) by the action of alkali on 1-acetylisatin and by Borsche and Jacobs (*Ber.*, 1914, **47**, 354) from malonic acid and isatin in acetic acid solution. The last reaction has now been found to take the same course in absence of solvents at 200°, and the identity of the product with that of Camps has been confirmed, even when it was purified by means of non-aqueous solvents to avoid the possibility of isomerisation during purification—a possibility that was overlooked by Borsche and Jacobs. This synthesis would appear to favour the indolinone structure (II) for the acid, which is reducible to a compound formerly described as " oxindole-3-acetic acid " (*vide infra*), but that the acid rightly receives the constitution (III) is shown by its methylation with methyl sulphate and alkali, or by the action of methyl iodide on its methyl ester, producing *methyl* 1-*methyl*-2-*quinolone*-4-*carboxylate* identical with that obtained by esterification of 1-methyl-2-quinolone-4-carboxylic acid. Borsche and Jacobs failed to effect methylation of the acid.

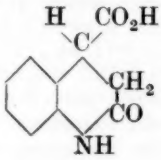
Just as 2-quinolone-4-carboxylic acid (III) is produced from isatin and malonic acid in boiling acetic acid solution by rupture of the indolinone ring and subsequent formation of the quinolone, so also is 1-methyl-2-quinolone-4-carboxylic acid obtained from 1-methylisatin and malonic acid. Borsche and Jacobs (*loc. cit.*), who examined this reaction in acetic acid at 100°, isolated β-carboxy-*o*-methylaminocinnamic acid (IV), but did not convert it into 1-methyl-2-quinolone-4-carboxylic acid. The latter acid, however, is formed under the above conditions, being the " amorphous product " neglected by these authors, and becomes the chief product when the reaction is carried out in boiling acetic acid. Its constitution is proved by its esterification to ethyl 1-methyl-2-quinolone-4-carboxylate identical with a specimen kindly supplied by Dr. Thielepape and prepared by dehydration of α-ethoxalyl-*N*-methylacetanilide (*Ber.*, 1922, **55**, 127). This ester is the only compound of those mentioned above whose synthesis excludes the possibility of its possessing an indolinone structure, and it had not



(IV.)



(V.)

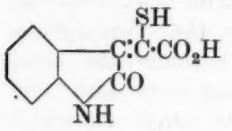


(VI.)

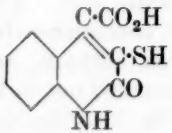
previously been prepared from the acid. The acid (IV) is not dehydrated by prolonged heating in a vacuum at 100—110°, but

above 120°, or in boiling acetic acid solution, ring closure takes place and 1-methyl-2-quinolone-4-carboxylic acid is formed, and this acid is not hydrated by crystallising from water. These facts appear to indicate that the acid (IV) possesses a maleinoid configuration, because the corresponding acids (I) and (III) are readily interconvertible.

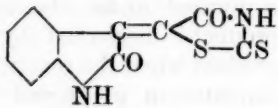
2-Quinolone-4-carboxylic acid is converted by acid or alkaline reducing agents into 2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid* (VI), and its methyl ester is reduced by aluminium amalgam in alcohol to the *methyl* ester of (VI), proving that the quinolone ring has remained intact during reduction. The acid (VI) is identical with the "oxindole-3-acetic acid" (V) prepared by Gränacher and Mahal (*Helv. Chim. Acta*, 1923, **6**, 467) by reduction of "oxindole-3-α-thiolacetic acid" (VII), which was obtained by alkaline hydrolysis of 3-rhodanylideneoxindole (IX). Under such conditions the lactam ring would be opened * and subsequent closure would, by analogy with the above cases, produce a thiolquinolone (VIII) reducible to 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid (VI). The quinolone structure of the thiol acid would account for the stability of the thiol group to ammonia, and is in accordance with its other reactions; a revision of the structural formulæ of its derivatives, however, is necessary. The product obtained by condensing the thiol acid with *o*-phenylenediamine was not dissolved by cold dilute alkalis, probably owing to internal salt formation.



(VII.)



(VIII.)



(IX.)

1-Methyl-2-quinolone-4-carboxylic acid is reduced to 2-*keto*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid*, m. p. 171°,

* It appears probable that when Thioindigo Scarlet R is hydrolysed by alkali a similar fission of the lactam ring occurs, since one of the products, which is described as oxindole-3-aldehyde (Friedländer and Kielbasinski, *Ber.*, 1911, **44**, 3101), has acidic properties and is similar to indole-3-carboxylic acid. This acid could be formed by such a fission followed by ring closure between the aldehydo- and the amino-group—the carboxyl group being unable to undergo condensation in presence of alkali.

The production of quinoline-4-carboxylic acids from sodium isatate and compounds containing the $-CO\cdot CH_2-$ group is also a result of the unequal competition between a carboxyl and an aldehydic group for condensation with the amino-group and does not prove the greater stability of the six-membered ring.

identical with the acid formed by methylating 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid (VI).

In the above cases where there is direct competition between two carboxyl groups for condensation with an amino-group, the production of the quinolone indicates that it is more stable than the indolinone. The preferential formation of the six-membered ring is in agreement with the theory of induced alternate polarities, but this theory would also predict the non-formation of all rings with an odd number of atoms (compare Flürscheim, *Chem. and Ind.*, 1925, **44**, 79).

The colour reaction of 3-methyl-2-indolinone and other oxindole derivatives with potassium dichromate and sulphuric acid (Brunner, *Monatsh.*, 1897, **18**, 536) is given also by the dihydroquinolone-carboxylic acids described in this paper. This fact, however, is not evidence against the quinolone structure of these substances, for the same reaction is given by acetanilide. The reaction is apparently more general than has been supposed, although it seems to be confined to compounds containing the $\cdot C_6H_4\cdot NH\cdot CO\cdot CHR\cdot$ group.

When 2-ketotetrahydroquinoline-4-carboxylic acid (VI) is heated with phosphorus pentachloride, dehydrogenation takes place and 2-chloroquinoline-4-carboxylic acid (Koenigs, *loc. cit.*) is produced. This result is confirmed by the formation of ethyl 2-quinolone-4-carboxylate from the product by the action of alcoholic sulphuric acid. Ethyl 2-chloroquinoline-4-carboxylate, obtained by Thielepape (*loc. cit.*) from ethyl 1-methyl-2-quinolone-4-carboxylate by the action of phosphorus pentachloride and oxychloride, was obtained in small yield under similar conditions from ethyl 2-quinolone-4-carboxylate, additional evidence for its structure thus being furnished. Attempts to replace the chlorine atom of 2-chloroquinoline-4-carboxylic acid by hydrogen and to oxidise 4-methylcarbostyril to the acid (III) were unsuccessful.

Isatin condenses with phenylacetic acid (Gysae, *Ber.*, 1893, **26**, 2484) and with its anhydride (Hübner, *Ber.*, 1908, **41**, 486) to give 3-phenyl-2-quinolone-4-carboxylic acid in each case (Borsche and Jacobs, *loc. cit.*). This acid has now been prepared by the action of hot dilute alkali on 1-*phenylacetylisatin*, obtained by the action of phenylacetyl chloride on 1-sodioisatin. The acid could not be esterified by alcoholic sulphuric acid, in agreement with the structure indicated, containing an ortho-substituent on each side of the carboxyl group.

Halogen Derivatives.

At the time when the available evidence seemed to indicate the indolinone structure for " oxindole-3-acetic acid," it was of interest

to prepare its iodo-derivatives on account of their possible similarity to thyroxin (Kendall, *Ind. Eng. Chem.*, 1925, **17**, 526; *J. Amer. Chem. Soc.*, 1926, **48**, 1384). The conclusive results of Harington (*Biochem. J.*, 1926, **20**, 300) showed, however, that no such similarity could exist.

6-Iodo-2-quinolone-4-carboxylic acid has been prepared by condensing 5-iodoisatin (Borsche and others, *Ber.*, 1924, **57**, 1770) with malonic acid, and is also formed by the action of iodine monochloride on 2-quinolone-4-carboxylic acid in acetic acid and of alkali on 5-*iodo*-1-*acetylisatin*.

2-Ketotetrahydroquinoline-4-carboxylic acid (VI) is not affected by iodine in presence of alkali, but is converted by the action of iodine monochloride in acetic acid solution into a 6(?)-iodo-derivative, the halogen atom of which is stable to alcoholic potash. The monohydrated form in which this derivative crystallises from water is probably the dicarboxylic acid produced by fission of the quinolone ring, for although it behaves as a monobasic acid on titration, as does also the acid (IV), it is dehydrated only in a vacuum at 100°. 2-*Aminophenylsuccinic acid* forms a lactam (VI) more readily than 5-*iodo*-2-*aminophenylsuccinic acid*, an open-ring structure being favoured by the presence of iodine in the benzene nucleus (compare Kendall, *loc. cit.*). 6-Iodo-2-quinolone-4-carboxylic acid also is formed, to the extent of 20%, when iodine monochloride acts on 2-ketotetrahydroquinoline-4-carboxylic acid in acetic acid solution at 100°, the product being characterised by conversion into its *methyl* and *ethyl* esters. Dehydrogenation therefore takes place in the 3 : 4-positions, and an iodine atom enters in the 6-position. A similar dehydrogenation of Kendall's oxindole-3-propionic acid appears much more probable than the imino-ring-structure he suggests.

Experimental.

2-*Quinolone*-4-*carboxylic Acid* (III).—(*a*) A solution of 10 g. of isatin, 0·5 g. of fused sodium acetate, and 7 g. of malonic acid in 50 c.c. of glacial acetic acid was heated for 2 hours. The crystals (8 g.) that separated were washed with alcohol and ether, and a portion for analysis was crystallised from alcohol and sublimed in a vacuum. The acid is more conveniently purified by decolorising an ammoniacal solution with carbon.

(*b*) To a boiling solution of 12 g. of sodium hydroxide in 750 c.c. of water, 25 g. of acetylisatin (or acetylisatic acid) were added and the boiling was continued for an hour. The hot solution was then acidified and the flocculent precipitate at once removed and purified as above. From the filtrate about 4 g. of isatin separated on

cooling. Concentrated or alcoholic alkali produces a greater proportion of isatin (compare Suida, *Ber.*, 1878, **11**, 586).

(*c*) Acetylisatin or acetylisatic acid (but *not* isatin) was converted into the above acid by heating it with crystalline sodium acetate (8 parts) until the solid mass began to fuse for the second time, the temperature being kept at 220° for 10 minutes. The aqueous extract was acidified and the precipitated acid purified as usual.

Only acetylisatic acid was produced by the action of boiling solutions of sodium carbonate, borate or acetate on acetylisatin, or by 1% sodium hydroxide solution at 90°.

The specimens of 2-quinolone-4-carboxylic acid prepared by the above methods melted at 343° (corr.), either alone or mixed (Found : C, 63·0, 63·5; H, 3·9, 3·9; N, 7·2. Calc. : C, 63·5; H, 3·7; N, 7·4%). The monohydrated form crystallises from hot water, in which it is slightly soluble, and behaves as a monobasic acid on titration. It is probably *o*-aminophenylfumaric acid.

The methyl and ethyl esters were formed on boiling alcoholic solutions of the acid with sulphuric acid for 1 hour; they were crystallised from alcohol or benzene. The methyl ester, m. p. 241°, prepared from specimens of the acid obtained by different methods, gave C, 65·0, 65·3; H, 4·35, 4·3 (Calc. : C, 65·0; H, 4·3%). The ethyl ester melted at 205° after sintering at 196°, as did that obtained by Koenigs by the action of ethyl iodide on the silver salt.

2-*Keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid* (VI) was prepared by the action of 100 g. of 4% sodium amalgam on a solution of 8 g. of the above acid in dilute alkali for 12 hours. The acid was liberated from the filtered solution and crystallised from hot water or alcohol. Zinc and acetic acid, or boiling hydriodic acid and phosphorus (contrast Koenigs, *loc. cit.*, for the action at 200°), or aluminium amalgam in neutral solution also effects the reduction. The monohydrated form (*o*-aminophenylsuccinic acid) obtained from aqueous solution behaves as a monobasic acid on titration (Equivalent, 209, 210. Calc. : 209). It is dehydrated in 48 hours in a vacuum at room temperature, or in 2 hours at 100° (Loss, 8·6. Calc. for $1H_2O$: 8·6%. Equiv., by titration in alcoholic solution : 190, 190·5. Calc. : 191). The lactam ring is rapidly formed when the disodium salt is acidified. The anhydrous acid melts at 220°, alone or mixed with a specimen of " oxindole-acetic acid " prepared by Gränacher and Mahal's method. The acid was not decomposed by concentrated hydrochloric acid below 200°, and at higher temperatures indefinite products were formed.

The *methyl* ester was formed by the action of methyl-alcoholic

sulphuric acid on the above acid, or by reducing methyl 2-quinolone-4-carboxylate with alcohol and aluminium amalgam or zinc and hydrochloric acid. Crystallised from benzene or alcohol, the specimens melted at 164°, separately or mixed (Found: C, 64·2; H, 5·3. $C_{11}H_{11}O_3N$ requires C, 64·4; H, 5·4%). The *ethyl* ester, m. p. 146°, was obtained by the action of alcoholic sulphuric acid on the acid.

1-Methyl-2-quinolone-4-carboxylic acid was obtained by heating 3·2 g. of 1-methylisatin with 2·1 g. of malonic acid in 10 c.c. of boiling acetic acid for 16 hours. A paste of crystals formed on cooling, and these were separated from the mother-liquor (containing β-carboxy-*o*-methylaminocinnamic acid) and recrystallised from absolute alcohol. Yield 1·6 g.; m. p. 250° (Found: C, 64·5; H, 4·5; equiv., 201, 200. Calc. for $C_{11}H_9O_3$: C, 65·0; H, 4·3%; equiv., 203). It was unchanged by alkali or water.

The ethyl ester was obtained by boiling the acid with alcoholic sulphuric acid. After crystallisation from benzene and alcohol it melted at 134—135°, alone or mixed with a specimen of ethyl 1-methyl-2-quinolone-4-carboxylate obtained from Dr. Thielepape.

The *methyl* ester was obtained by esterification, and also by heating 4 g. of 2-quinolone-4-carboxylic acid (III) in 30 c.c. of methyl alcohol with 4 g. of methyl sulphate for 4 hours, then adding 2 g. of sodium hydroxide and heating for a further 2 hours. The cold product was diluted with water and the crystals that separated were dried and extracted with hot benzene. The residue, and the product separating from the extract on cooling, was methyl 2-quinolone-4-carboxylate. By evaporating the benzene solution and crystallising the residue from a little methyl alcohol, *methyl 1-methyl-2-quinolone 4-carboxylate* was obtained, m. p. 120° (Found: C, 66·2; H, 5·1. $C_{12}H_{11}O_3N$ requires C, 66·4; H, 5·1%). A small yield of this ester was obtained by heating methyl 2-quinolone-4-carboxylate with methyl iodide for 48 hours at 100°.

β-Carboxy-*o*-methylaminocinnamic acid (IV) was obtained by heating 1-methylisatin (4·5 g.) and malonic acid (3·7 g.) with 5 c.c. of acetic acid at 100° for 48 hours. A small quantity of 1-methyl-2-quinolone-4-carboxylic acid was removed, and the aqueous solution concentrated in a vacuum; the dicarboxylic acid then separated. It melts at 163°, is much more soluble in water or alcohol than the quinolone, and behaves as a monobasic acid on titration (Equiv., 221. Calc.: 221).

2-Keto-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid is formed by reduction of 1-methyl-2-quinolone-4-carboxylic acid (IV) in dilute alkali by sodium amalgam, and also by treating a solution of 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid (VI

(2·5 g.) in 10 c.c. of 10% caustic soda with excess of methyl sulphate (seven portions of 1 c.c. each) with shaking. The product is heated with excess of 20% sodium hydroxide solution (30 c.c.) and acidified. The oil which separates is crystallised from water, and then melts at 171° (Found: C, 64·5; H, 5·2. $C_{11}H_{11}O_3N$ requires C, 64·4; H, 5·3%).

The *methyl* ester, m. p. 80°, is obtained when methyl 1-methyl-2-quinolone-4-carboxylate is reduced in alcoholic solution by aluminium amalgam.

1-*Phenylacetylisatin* was obtained by heating sodioisatin (Heller, *Ber.*, 1907, **40**, 1294) with a benzene solution of an equal weight of phenylacetyl chloride (prepared by heating the acid with excess of thionyl chloride at 100° for an hour and rectifying the product in a vacuum) for an hour. The mixture was filtered hot, and the residue of sodium chloride extracted several times with boiling benzene. 1-*Phenylacetylisatin* separated from the combined filtrates and was recrystallised from benzene–petrol; m. p. 188° (Found: C, 72·0; H, 4·6. $C_{16}H_{11}O_3N$ requires C, 72·4; H, 4·2%).

3-Phenyl-2-quinolone-4-carboxylic acid was formed when the above compound (1·1 g.) was added to a hot solution of 0·5 g. of sodium hydroxide in 20 c.c. of water. After 5 minutes' boiling the deep red solution became pale yellow and the acid was liberated and crystallised from alcohol. It melted at 295°, alone or mixed with the acid obtained by Gysae (*loc. cit.*) from isatin and phenylacetic acid (Found: C, 72·7; H, 4·4. Calc.: C, 72·4; H, 4·2%). The acid was not obtained by heating a mixture of phenylacetic acid (5 g.), isatin (5 g.), and sodium hydroxide (5 g.) in 40 c.c. of water for 12 hours.

The *quinoxaline* derivative of 3-thiol-2-quinolone-4-carboxylic acid (VIII) (the "oxindole-3-thiolacetic acid" of Gränacher and Mahal) was obtained by heating the acid with 20% excess of *o*-phenylenediamine for 24 hours in methyl or ethyl alcoholic solution until hydrogen sulphide ceased to be evolved. The insoluble, brown, amorphous product was purified by extracting soluble matter with more alcohol in a Soxhlet apparatus. It was insoluble in cold alkalis, but dissolved in boiling sodium hydroxide. The combined alcohol could not be removed in a vacuum without decomposition, but was detected qualitatively (Found: C, 67·2, 67·8; H, 4·7, 5·2. $C_{16}H_{11}O_2N_3,C_2H_5{\cdot}OH$ requires C, 66·9; H, 5·2%. Found: C, 66·4; H, 4·5. $C_{16}H_{11}O_2N_3,CH_3{\cdot}OH$ requires C, 66·0; H, 4·8%).

2-Chloroquinoline-4-carboxylic acid (2-chlorocinchoninic acid) was obtained when 2-quinolone-4-carboxylic acid or its dihydro-derivative (VI) (5 g.) was heated with phosphorus pentachloride

(25 g.) for 1 hour at 120°, and finally to 150° to remove phosphorus oxychloride. The products after reprecipitation from dilute sodium carbonate solution and crystallisation from alcohol, were identical, melting at 196—200° (decomp.) (Thielepape, *Ber.*, 1922, **55**, 133). On esterification with ethyl alcohol and sulphuric acid, each gave ethyl 2-quinolone-4-carboxylate (Found : C, 65·9; H, 5·2. Calc. : C, 66·3; H, 5·1%).

Ethyl 2-chloroquinoline-4-carboxylate, m. p. 63°, was, however, formed by heating ethyl 2-quinolone-4-carboxylate with phosphorus pentachloride and oxychloride under the conditions described by Thielepape (*loc. cit.*) for its production from ethyl 1-methyl-2-quinolone-4-carboxylate. It was separated from unchanged ester by its greater solubility in benzene.

5-Iodoisatin (compare *Ber.*, 1924, **57**, 1770) was formed by heating a concentrated solution of isatin and a 10% excess of 2*N*-iodine monochloride solution in glacial acetic acid at 100° for 4 hours. Scarlet crystals (m. p. 285°) separated and were washed with alcohol or acetone. The golden-yellow (enolic ?) form (Morton and Rogers, J., 1925, **127**, 2699) crystallised from a solution of the scarlet form in alkali on acidification, but was reconverted into the scarlet form on recrystallisation. The colour, therefore, probably depends on the state of division.

A di-iodo-derivative was not formed by using excess of iodine monochloride.

5-*Iodo*-1-*acetylisatin* separated when a solution of 10 g. of 5-iodoisatin in 50 c.c. of acetic anhydride which had been boiled for 1 hour was cooled. The golden crystals, m. p. 195°, were readily soluble in alcohol, less so in cold benzene or ether (Found : C, 37·5; H, 2·1. $C_{10}H_6O_3NI$ requires C, 38·1; H, 1·9%).

6-Iodo-2-quinolone-4-carboxylic acid was prepared by boiling a solution of 5-iodoisatin (8 g.) and malonic acid (8 g.) in acetic acid (400 c.c.) for 5 hours. The solid which separated (6 g.) was washed with acetone and recrystallised from boiling alcohol. The acid is very slightly soluble in organic solvents and does not melt below 300° (Found : C, 38·1; H, 2·3; N, 4·4. Calc. : C, 38·1; H, 1·9; N, 4·4%). The same acid is formed by boiling 5-iodo-1-acetylisatin (5 g.) with 1% sodium hydroxide solution (250 c.c.) for 1 hour. The product is freed from 5-iodoisatin by solution in dilute ammonia. Its ammonium salt crystallises from concentrated ammonia solutions.

6-Iodo-2-quinolone-4-carboxylic acid was also obtained when a solution of iodine monochloride (10 g.) and 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid (10 g.) (or 2-quinolone-4-carboxylic acid) in acetic acid (100 c.c.) was boiled for 4 hours.

The heavy, crystalline precipitate (3·5 g.) was washed with alcohol and ether (Found: C, 38·4; H, 2·0%). The iodine atom was removed on reduction with sodium amalgam. The above products were characterised, and their identity proved, by esterifying them for 8 hours with alcoholic sulphuric acid. The esters can be crystallised from hot alcohol; the *methyl* ester has m. p. 261° (Found: C, 39·9; H, 2·8. $C_{11}H_8O_3NI$ requires C, 40·1; H, 2·4%) and the *ethyl* ester has m. p. 223° (Found: C, 42·1; H, 3·0. $C_{12}H_{10}O_3NI$ requires C, 42·0; H, 2·9%).

6(?)-*Iodo*-2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid* was obtained by the action of 2*N*-iodine monochloride solution (12·8 c.c.) on a solution of the parent acid (5 g.) in acetic acid (50 c.c.) during 48 hours at room temperature. The solvent was removed in a vacuum on the water-bath, and the gummy residue boiled with water and crystallised from alcohol or 50% acetic acid. The monohydrated acid (5-*iodo*-2-*aminophenylsuccinic acid*) thus obtained melts at 180° if rapidly heated, but at 208° (the m. p. of the anhydrous acid) when slowly heated. The open-ring form is stable at 100° at atmospheric pressure, but is dehydrated at 110° at 15 mm. pressure (Found: C, 35·9, 35·9; H, 3·2, 3·4; loss on drying, 5·2. $C_{10}H_8O_3NI,H_2O$ requires C, 35·8; H, 3·2; H_2O, 5·3%). Both the hydrated and the anhydrous acid are monobasic under all conditions (Equiv.: found, 330 and 312, respectively. Calc.: 335 and 317). The *ethyl* ester has m. p. 169° (Found: C, 41·2; H, 3·1. $C_{12}H_{12}O_3NI$ requires C, 41·7; H, 3·5%).

6(?)-*Bromo*-2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid* was obtained by heating equimolecular quantities of 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid and bromine in acetic acid solution at 100° for 8 hours and isolated similarly to the iodo-derivative. It melts at 191° (Found, in material dried at 100°: C, 44·4; H, 3·4. $C_{10}H_8O_3NBr$ requires C, 44·4; H, 3·0%).

6-*Iodo*-3-*phenyl*-2-*quinolone*-4-*carboxylic acid* was prepared by heating 5-iodoisatin (5 g.) with phenylacetic acid (5 g.) and fused sodium acetate (0·2 g.) at 190—240° for 1 hour. The product, after being boiled with acetic acid, was crystallised from acetone. It did not melt below 300° and was not esterified by heating for 24 hours with alcoholic sulphuric acid (Found: C, 49·0; H, 2·6. $C_{16}H_{10}O_3NI$ requires C, 49·1; H, 2·3%). This acid and its bromine analogue (described by Gysae, *loc. cit.*, as "brom-isaphensaure") can be reduced by sodium amalgam to 2-keto-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, m. p. 202°, identical with that obtained by reduction of the unhalogenated acid and described by Gysae as "dihydro-isaphensaure."

In conclusion, the author expresses his thanks to Dr. R. H. Pickard, F.R.S., and Dr. J. Kenyon for the facilities provided and for their criticism of this paper, and to Messrs. C. F. Boehringer and Sons, Mannheim-Waldhof, for a gift of 3-methylindolinone.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, July 19th*, 1926.]

CCCLXXXVIII.—*Nitration of 2-, 3-, and 4-Phenylpyridines.*

By ROBERT FORSYTH and FRANK LEE PYMAN.

FORSYTH, NIMKAR, and PYMAN (this vol., p. 800) suggested as an explanation of the facts that nitration leads mainly to meta-substitution in 2-phenyl-4 : 5-dihydroglyoxaline (I), but mainly to para-substitution in 2-phenylglyoxaline (II), that the effect of the

(I.) $\begin{matrix} CH_2{\cdot}NH \\ | \\ CH_2{-}N \end{matrix}\!\!>\!CPh$ $\qquad$ $\begin{matrix} CH{\cdot}NH \\ \| \\ CH{-}N \end{matrix}\!\!>\!CPh$ (II.)

nitrogen atoms in the latter compound was suppressed, the glyoxalinium ion behaving as an aromatic complex as a whole and having a para-directive effect like the phenyl group in diphenyl. In order to test this hypothesis, the nitration of 2-, 3-, and 4-phenylpyridines was proposed with the view of determining whether the pyridinium residue had mainly an *op*-directive effect in all cases, or, if not, how far the position of the nitrogen atom relative to the phenyl group affected the result. This has now been done by the method used in the previous cases (addition of the nitrate of the base to sulphuric acid), and the yields of pure or nearly pure isomerides isolated were as follows :

	Nitro-derivatives.		
	o.	*m*.	*p*.
2-Phenylpyridine	5·1	34·9	42·3%
3- „	—*	—*	64·3
4- „	12·7	28·5	38·0

* Not determined.

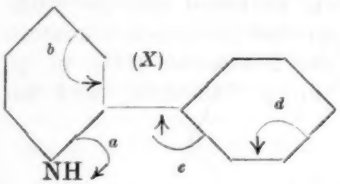
After allowance is made for losses in manipulation, it is clear that *op*-substitution predominates in all cases, although a considerable amount of *m*-substitution occurs in the nitration of 2- and 4-phenylpyridines. Evidence of an alternating effect is seen in the relative yields of the *p*-nitro-compounds. At the Society's meeting on June 17th, one of us invited forecasts of these results, and has received them from three chemists.

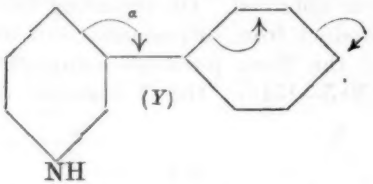
Dr. Flürscheim writes : "I predict the following : (1) the percentage of *op*-compound *formed* (calculated on the total $o + p +$

m formed) will be in the order 3>4>2; (2) in 3-phenylpyridine *op*-substitution will be practically exclusive. For the 3-compound, I am able to make this absolute prediction, because here substitution depends practically only on the affinity demand of the 3-carbon atom in the pyridine ring, which is greater than that of hydrogen, both in the free base and in the salt. For the 2- and 4-compounds, I am only able to make the above relative prediction, because here substitution depends both on the degree of hydrolysis and of electrolytic dissociation of the salt, both of which I can foresee relatively, whereas their absolute magnitude is unknown."

Professor Ingold writes: "I would expect the proportion of *meta*- in the mono-nitration product of 2-, 3-, and 4-phenylpyridine to stand in the order 2>4>3. Even in 2-phenylpyridine I would not expect a very large *m*-content, say 50% as a maximum. In the case of the 3-derivative, I should think the *m*-content would be almost zero, or, at any rate, quite small, and I would expect the *para*- to be the main product."

Professor Robinson writes: "The substituting agent is kationoid and consequently the distributed positive charge on the phenylpyridinium ions should reduce the reactivity even of the phenyl group. Substitution in the benzene nucleus, which will obviously be preferentially attacked, should be influenced by (1) the general polar effect of the phenylpyridinium ions, (2) the crotonoid systems in the 2- and 4-phenylpyridines, and (3) butadienoid conjugation of the two nuclei. All these effects are weak; for example, the crotonoid system in 2-phenylpyridine is weak because, as illustrated in the annexed expression (*X*), the original electron displacement (*a*) is doubtless more readily accommodated (*b*) within the nucleus than by the changes (*c*) and (*d*). On the other hand, the butadienoid

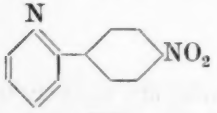




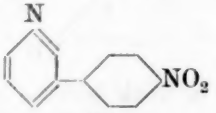
conjugation (*Y*) should be weak because electrons are unlikely to start the process (α) in view of the charge on the pyridine nucleus and the high degree of stability of the aromatic sextet in pyridine. If we consider *m*- as against combined *o*-*p*, then, on account of (1) above, the percentage of *m*-nitrophenylpyridines obtained should be in the order 2->3->4-phenylpyridine. On account of (2), the percentage of *m*-substituted derivatives should be in the order 2->4->3-phenylpyridine, and, finally, the factor (3) gives 2->4->3-

phenylpyridine. Certainly, therefore, the percentage of *m*-nitrophenylpyridine obtained should be highest in the case of the 2-phenylpyridine and probably after this would come 4-phenylpyridine. It is also probable that the gap separating 2- and 4- will be greater than that between 3- and 4-. It is not possible to deduce from the electronic theories what the relation between *m*- and *o*-*p* should be in the individual cases, because pyridyl (β) stands at the end of a series of aromatic groups and the extrapolation involved is scarcely justifiable. Analogies suggest, however, that *o*-*p*-substitution should predominate in 3-phenylpyridine."

Considerable difficulty was encountered in preparing quantities of the starting materials. 2-Phenylpyridine was first prepared by Skraup and Cobenzl (*Monatsh.*, 1883, **4**, 472) by the decarboxylation of its dicarboxylic acid, which, they state, they obtained by the oxidation of α-naphthaquinoline in the same way as they had prepared its isomeride by the oxidation of β-naphthaquinoline. In our hands, α-naphthaquinoline proved to be very resistant to warm permanganate, and in several experiments a large proportion of this substance was recovered unchanged, but none of the dicarboxylic acid was obtained. Attempts were then made—on the lines of Decker and Pschorr's syntheses (*Ber.*, 1904, **37**, 3397) of 1-alkyl*iso*quinolines—to prepare 2-phenylpyridine methobromide by the action of magnesium phenyl bromide upon *N*-methyl-α-pyridone, but these were unsuccessful. Finally, we had recourse to the method of Kühling (*Ber.*, 1895, **28**, 523; 1896, **29**, 165), who obtained 2-*p*-nitrophenylpyridine in "good yield" by the action of acetic acid and acetyl chloride upon sodium *p*-nitrobenzene*iso*diazotate in pyridine, reduced this to the amine, and eliminated the amino-group by means of nitrous acid and alcohol, when 2-phenylpyridine was obtained. On repeating this work, we found that the crude product from nitrosoamine-salt and pyridine contained a mixture of the three p-*nitrophenylpyridines*, the 2-*isomeride* (III), m. p. 130·5—131·5°, the 3-*isomeride* (IV), m. p. 148—149°, and the



(III.)



(IV.)

(V.)

4-*isomeride* (V), m. p. 123—124°, being isolated in yields of 15, 5, and 2%,* respectively, after a long process of crystallisation as

* For comparison, it may be noted that solid benzenediazonium chloride reacts with excess of pyridine to give 2-phenylpyridine in 18% yield, and a difficultly separable mixture of this with 4-phenylpyridine in 3% yield (Möhlau and Berger, *Ber.*, 1893, **26**, 1994).

base, hydrochloride, and nitrate. The preparation of quantities of the 2-, 3-, and 4-phenylpyridines (VIII), and at the same time the determination of the constitutions of the three nitro-compounds, was effected by reducing each to the amine [2-, 3-, and 4-p-*aminophenylpyridines* (VI)], diazotisation of the amine, and reduction of the diazonium salt to the hydrazine [2-, 3-, and 4-p-*hydrazinophenylpyridines* (VII)], followed by oxidation of the hydrazine with cupric acetate.

$$\underset{\text{(VI.)}}{C_5H_4N\cdot C_6H_4\cdot NH_2} \longrightarrow \underset{\text{(VII.)}}{C_5H_4N\cdot C_6H_4\cdot NH\cdot NH_2} \longrightarrow \underset{\text{(VIII.)}}{C_5H_4N\cdot C_6H_5}$$

The 2- and 3-phenylpyridines were identified by reference to the properties of their salts, and 4-phenylpyridine by direct comparison with a specimen prepared by Hantzsch's method (*Ber.*, 1884, **17**, 1512).

Reference to the melting points given above shows that Kühling's 2-*p*-nitrophenylpyridine, which sintered from 109° and melted, not sharply, at 117°, was a mixture. It doubtless consisted mainly of the 2-isomeride with some of the 3-isomeride, which would not be removed from the first by the methods which he employed. His aminophenylpyridine base has a higher m. p. than pure 2-*p*-aminophenylpyridine, but agrees in m. p. with 3-*p*-aminophenylpyridine containing solvent of crystallisation. The method which he employed for eliminating the amino-group is unsatisfactory in this case, for on boiling 2-*p*-aminophenylpyridine dihydrochloride with alcohol and amyl nitrite, only a poor yield of 2-phenylpyridine is obtained owing to the formation of a considerable quantity of 2-p-*ethoxyphenylpyridine*, $C_5H_4N\cdot C_6H_4\cdot OEt$.

The orientation of the products of nitration of the three phenylpyridines was determined as follows: the three *p*-nitro-compounds were recognised through their identity with products of interaction of sodium *p*-nitrobenzene*iso*diazotate and pyridine, the 2- and 4-m-*nitrophenylpyridines* through the formation of *m*-nitrobenzoic acid on oxidation of their methosulphates by permanganate, and the 2- and 4-o-*nitrophenylpyridines* by difference.

EXPERIMENTAL.

The p-*Nitrophenylpyridines.*—The sodium *p*-nitrobenzene*iso*diazotate from 13·8 g. of *p*-nitroaniline was washed with brine, dried at 100°, finely powdered, and covered with pure pyridine (80 c.c.) in a 1-litre beaker. To the nearly complete, dark brown solution thus obtained, glacial acetic acid (60 c.c.), quickly followed by acetyl chloride (10 c.c.), was added, a vigorous reaction taking place. After a few minutes, the product was diluted with water (1 l.), and the insoluble matter collected. This was extracted with hot

5*N*-hydrochloric acid (500 c.c.), and the extract basified with ammonia; 9·5 g. of crude bases, crystalline but sticky, were then precipitated.

The crude bases (200 g.) prepared in this way from 289·8 g. of *p*-nitroaniline were dissolved in hot 5*N*-hydrochloric acid (1·2 l.) and the solution was digested with charcoal, filtered, and kept; the hydrochlorides of the 2- and 4-isomerides that crystallised were collected, and further crops were obtained by concentration of the mother-liquors (Mother-liquor M). The bases regenerated from the crystalline hydrochlorides were crystallised fractionally from alcohol; the 2-isomeride was then obtained in a nearly pure state. Its purification was completed by further crystallisation as hydrochloride from 5*N*-hydrochloric acid, followed by crystallisation of the base from alcohol. The fraction of the bases most soluble in alcohol gave, on crystallisation from 5*N*-hydrochloric acid, the hydrochloride of the 4-isomeride. After recrystallisation as hydrochloride, and then as base from acetone, the 4-isomeride was obtained in a pure state as regards its m. p., but both the base and the hydrochloride prepared in this way had a deep yellow colour, which was absent from 4-*p*-nitrophenylpyridine, and its hydrochloride, prepared by the nitration of 4-phenylpyridine. The mother-liquor M gave, when basified, a sticky product which was extracted with cold ether, and thus separated into a readily soluble fraction (from which further small quantities of the three isomerides were isolated) and a sparingly soluble crystalline powder, which gave the pure 3-isomeride after crystallisation as base from alcohol, as nitrate from *N*-nitric acid, and again as base from alcohol. After a long process of fractionation on these lines, the 2-, 3-, and 4-*p*-nitrophenylpyridines were isolated in a pure state in quantities of 64·7, 22·2, and 10·3 g., respectively, the yields being 15·4, 5·3, and 2·4%, respectively, of the theoretical yields, calculated on the *p*-nitroaniline used.

2-Phenylpyridine and its Derivatives.

2-p-*Nitrophenylpyridine* crystallises from alcohol in nearly colourless needles, m. p. 130·5—131·5° (corr.). It is insoluble in water, sparingly soluble in alcohol, acetone, or ether, but readily soluble in chloroform (Found : C, 66·1; H, 4·2; N, 14·1. $C_{11}H_8O_2N_2$ requires C, 66·0; H, 4·0; N, 14·0%). The *hydrochloride* crystallises from 5*N*-hydrochloric acid in nearly colourless, prismatic needles containing $2H_2O$, which is lost in a vacuum over sulphuric acid. The dried salt has m. p. 185—186° (corr.) (Found : loss, 12·7. $C_{11}H_8O_2N_2,HCl,2H_2O$ requires $2H_2O$, 13·2%. Found, in dried salt : Cl, 15·0. $C_{11}H_8O_2N_2,HCl$ requires Cl, 15·0%). It slowly loses hydrogen chloride at 100° and dissociates on treatment with

water, giving a copious deposit of the base. The latter behaviour is not shown by the nitrate of the 3-isomeride or the hydrochloride of the 4-isomeride, but aqueous solutions of the nitrate of the 3-isomeride give a faint crystalline precipitate.

2-p-*Aminophenylpyridine*.—2-*p*-Nitrophenylpyridine (20 g.) was reduced by tin foil (40 g.) and concentrated hydrochloric acid (120 c.c.). The solution was diluted with water, and concentrated after removal of tin by hydrogen sulphide, 2-*p*-aminophenylpyridine dihydrochloride (20·4 g.; yield, 84%) separating.

2-p-*Aminophenylpyridine* crystallises from ether in nearly colourless, elongated prisms or from alcohol in quadrilateral prisms, m. p. 97—98° (corr.). It is insoluble in water, sparingly soluble in ether, and easily soluble in alcohol (Found: C, 77·5; H, 5·7. $C_{11}H_{10}N_2$ requires C, 77·7; H, 5·9%). The *dihydrochloride* crystallises from dilute hydrochloric acid in colourless, felted needles, which are readily soluble in water, giving a yellow solution, but very sparingly soluble in alcohol. It is anhydrous and does not melt at 310° (Found: C, 54·3; H, 4·9. $C_{11}H_{10}N_2,2HCl$ requires C, 54·3; H, 4·9%). The *picrate* crystallises from alcohol in elongated plates, m. p. 218—219° (decomp.; corr.).

2-p-*Hydrazinophenylpyridine*.—2-*p*-Aminophenylpyridine dihydrochloride (20 g.) in water (180 c.c.) and concentrated hydrochloric acid (80 c.c.) was diazotised at 15° by sodium nitrite (5·9 g.) in aqueous solution. To this, a cold solution of hydrated stannous chloride (75 g.) in concentrated hydrochloric acid (150 c.c.) was added, and after keeping for 1 hour, the tin was removed by hydrogen sulphide. The solution was concentrated and basified with ammonia; the bulk of the hydrazine (11·7 g.; m. p. 112—113°) then separated as an oil which quickly became crystalline. The filtrate was extracted with ether, and the extract, after being concentrated, deposited a further 0·2 g. of the hydrazine, of which the total yield is thus 78% of the theoretical.

2-p-*Hydrazinophenylpyridine* crystallises from alcohol in clear, nearly colourless, well-formed plates, m. p. 117° (corr.) after softening a few degrees lower. It is insoluble in water, soluble in alcohol, and sparingly soluble in ether (Found: C, 71·5; H, 6·0. $C_{11}H_{11}N_3$ requires C, 71·4; H, 6·0%).

2-*Phenylpyridine*.—To 2-*p*-hydrazinophenylpyridine (11·7 g.; m. p. 112—113°) dissolved in 5*N*-acetic acid (80 c.c.), powdered cupric acetate (27 g.) was added and the product was basified and distilled with steam. Ether extracted from the distillate 2-phenylpyridine (7·3 g.), which was converted into the nitrate and crystallised from absolute alcohol, 10·1 g. of the pure salt being obtained (yield, 73%).

2-*Phenylpyridine nitrate* crystallises from absolute alcohol in large, colourless, elongated prisms, m. p. 115—117° (corr.). It is anhydrous and easily soluble in water, but sparingly soluble in cold absolute alcohol (Found : C, 60·4 ; H, 4·7. $C_{11}H_9N,HNO_3$ requires C, 60·5 ; H, 4·6%). 2-Phenylpyridine was identified through its properties and those of its picrate and chloroplatinate. The base was an oil, volatile with steam. The picrate crystallised from alcohol in yellow prisms, m. p. 176—177° (corr.) (Found : C, 52·9 ; H, 3·1. Calc. : C, 53·1 ; H, 3·1%). Skraup and Cobenzl (*loc. cit.*) give m. p. 169—172° ; Leben (*Ber.*, 1896, **29**, 1673) gives m. p. 175°. The chloroplatinate crystallised from dilute hydrochloric acid in elongated plates, containing $2H_2O$, m. p. (after drying) 209° (decomp. ; corr.) (Found, in air-dried salt : loss at 100°, 5·4. Calc. : 4·8%. Found, in dried salt : Pt, 27·2. Calc. : Pt, 27·1%). Skraup and Cobenzl and also Leben state that this salt crystallises with $2H_2O$, and the latter gives m. p. 204°.

2-p-*Ethoxyphenylpyridine*.—Finely-powdered 2-*p*-aminophenylpyridine dihydrochloride (7·5 g.), absolute alcohol (75 c.c.), and amyl nitrite (10 c.c.) were boiled gently on the water-bath during 3 hours, in the course of which another 8 c.c. of amyl nitrite were added. Hydrochloric acid was added, the alcohol distilled off, and amyl alcohol removed in a current of steam. The liquor was then basified and distilled with steam fractionally ; mixtures of 2-phenylpyridine with 2-*p*-ethoxyphenylpyridine passed over, the former (liquid) predominating in the earlier runnings and the latter (solid) in the later. Further quantities of 2-*p*-ethoxyphenylpyridine were obtained by extracting the distillation residue with ether, and eventually 1·1 g. (yield 18%) were obtained pure. The 2-phenylpyridine was converted into picrate, and after many crystallisations from alcohol 2·95 g. (yield 25%) of this salt were obtained pure.

2-p-*Ethoxyphenylpyridine* crystallises from ether in large, colourless prisms, m. p. 74—75° (corr.), which are insoluble in water but readily soluble in alcohol or ether (Found : C, 78·2 ; H, 6·5. $C_{13}H_{13}ON$ requires C, 78·4 ; H, 6·5%). The *picrate* crystallises from alcohol in yellow, woolly needles, m. p. 168—170° (corr.) (Found : C, 53·3 ; H, 3·5 ; N, 13·1. $C_{13}H_{13}ON,C_6H_3O_7N_3$ requires C, 53·3 ; H, 3·7 ; N, 13·1%).

Nitration of 2-Phenylpyridine.—2-Phenylpyridine nitrate (12 g.) was added gradually to concentrated sulphuric acid (24 c.c.) cooled with water. After keeping for 5 minutes, the product was heated for ½ hour at 100°, then diluted with water (120 c.c.) and precipitated fractionally with 5*N*-ammonia. First, pure 2-*p*-nitrophenylpyridine separated from the liquor while still hot in three crops

amounting to 3·95 g., m. p. 130—131°. After cooling and addition of more ammonia, another three crops amounting to 4·07 g., m. p. about 62—64°, separated; the final crop, collected by ether, was 2·75 g., m. p. about 35°. When the 4·07 g. were crystallised from 40 c.c. of 5*N*-nitric acid, the nitrate of the *m*-isomeride separated, and the bases regenerated from the mother-liquors readily gave more of the *p*-isomeride on crystallisation from alcohol. The 2·75 g. also gave a quantity of the nitrate of the *m*-isomeride on crystallisation from 27 c.c. of 5*N*-nitric acid, but the bases regenerated from these mother-liquors contained little of the *p*-isomeride. After the *p*- and *m*-isomerides had been removed as completely as possible by these means, the residual bases were precipitated fractionally from dilute hydrochloric acid by ammonia; mixtures of the *p*- and *m*-isomerides were precipitated first, followed by the crude *o*-base. The *p*-isomeride was finally purified by crystallisation from alcohol; the *m*-isomeride by recrystallisation of its nitrate from 5*N*-nitric acid, followed by crystallisation of the base from alcohol; and the *o*-isomeride by recrystallisation from ether. The yields were as follows: *p*-, 4·61 g. pure + 0·05 g., m. p. 125—128° (42·3%); *m*-, 3·82 g. pure + 0·02 g., m. p. 68—70° (34·9%); *o*-, 0·52 g. pure + 0·04 g., m. p. 57—59° (5·1%). In addition, a final residue of base (0·6 g., m. p. 35—37°, yield 5·4%) doubtless consisted largely of the *o*-isomeride. The *p*-isomeride was identified by comparison and by the mixed-m. p. method with 2-*p*-nitrophenylpyridine prepared from *p*-nitroaniline.

2-m-*Nitrophenylpyridine* crystallises from alcohol in very pale yellow, prismatic needles, m. p. 73—74° (corr.) (Found: C, 65·9; H, 4·0. $C_{11}H_8O_2N_2$ requires C, 66·0; H, 4·0%). It is insoluble in cold water, sparingly soluble in cold alcohol, and soluble in ether. The *nitrate* crystallises from 5*N*-nitric acid in colourless needles, m. p. 193° (corr.) (Found, in air-dried salt: loss at 110°, 2·0%. Found, in dried salt: N, 16·0. $C_{11}H_8O_2N_2,HNO_3$ requires N, 16·0%). The orientation of the nitro-group was determined by heating 2-*m*-nitrophenylpyridine (0·5 g.) with methyl sulphate (0·5 c.c.) for 10 minutes at 100°, and oxidising the methosulphate (which crystallised readily) in alkaline solution with potassium permanganate (2·5 g.); 0·08 g. of *m*-nitrobenzoic acid, m. p. 140—141°, alone or mixed with a genuine specimen, was then obtained.

2-o-*Nitrophenylpyridine* crystallises from ether in large, colourless, quadrilateral tablets, m. p. 60—61° (corr.) (Found: C, 66·0; H, 4·0. $C_{11}H_8O_2N_2$ requires C, 66·0; H, 4·0%). It is insoluble in cold water, but readily soluble in alcohol or ether.

3-Phenylpyridine and its Derivatives.

3-p-*Nitrophenylpyridine* crystallises from alcohol in pale buff needles, m. p. 148—149° (corr.) (Found: C, 66·0; H, 4·1; N, 14·0. $C_{11}H_8O_2N_2$ requires C, 66·0; H, 4·0; N, 14·0%). It is insoluble in water, sparingly soluble in alcohol, acetone, or ether, and readily soluble in chloroform. The *nitrate* crystallises from *N*-nitric acid in anhydrous, cream-coloured, silky needles, m. p. 198° (corr.) (Found: N, 16·0. $C_{11}H_8O_2N_2,HNO_3$ requires N, 16·0%).

3-*p*-Nitrophenylpyridine was converted into 3-phenylpyridine through the amine and hydrazine, the same methods and proportions being used in each operation as in the case of the corresponding 2-isomerides.

3-p-*Aminophenylpyridine* was isolated as dihydrochloride in 89% yield. The base crystallises from moist alcohol in colourless plates, m. p. 102—104° (corr.), containing solvent of crystallisation, and after drying at 100° (loss, 9·9, 10·2. $C_{11}H_{10}N_2,H_2O$ requires H_2O, 9·6%) has m. p. 118—120° (corr.) (Found, in dried base: C, 77·6; H, 5·9. $C_{11}H_{10}N_2$ requires C, 77·7; H, 5·9%). The *dihydrochloride* crystallises from dilute hydrochloric acid in small, colourless needles, m. p. *ca.* 310° (decomp.; corr.). It is readily soluble in water, and sparingly soluble in alcohol (Found, in air-dried salt: loss at 110°, 3·7. $C_{11}H_{10}N_2,2HCl,\frac{1}{2}H_2O$ requires H_2O, 3·6%. Found, in dried salt: Cl, 29·1. $C_{11}H_{10}N_2,2HCl$ requires Cl, 29·2%). The *picrate* is precipitated in yellow needles, m. p. 185—188°, when alcoholic solutions of the base (1 mol.) and picric acid (2 mols.) are mixed, but when this product is boiled with much alcohol it is converted into orange needles, m. p. 219—220° (corr.), which are very sparingly soluble in hot alcohol and presumably represent a monopicrate.

3-p-*Hydrazinophenylpyridine* was isolated as base, m. p. 153—154°, in 70% yield. It crystallises from alcohol in colourless, anhydrous leaflets, m. p. 156—157° (corr.) (Found: C, 71·2; H, 6·1. $C_{11}H_{11}N_3$ requires C, 71·4; H, 6·0%). It is insoluble in water and sparingly soluble in ether or cold alcohol. 3-Phenylpyridine was isolated in 74% yield. It was identified through its properties and those of its picrate. The base was an oil volatile with steam, whilst the picrate crystallised from alcohol in woolly, yellow needles, m. p. 162—164° (corr.). Skraup and Cobenzl (*loc. cit.*) give m. p. 161—163·5°; Ciamician and Silber (*Ber.*, 1887, **20**, 191) give m. p. 162—163°. The *nitrate* crystallises from absolute alcohol in colourless, anhydrous prisms, m. p. 78—80° (corr.) (Found: N, 13·1, 13·0. $C_{11}H_9N,HNO_3$ requires N, 12·8%). It is very easily soluble in water or hot alcohol.

Nitration of 3-*Phenylpyridine*.—3-Phenylpyridine nitrate (6·1 g.) was added gradually to concentrated sulphuric acid (12·5 c.c.), cooled with water. After being kept for 5 minutes, the product was heated for ½ hour at 100°, then diluted with water and precipitated fractionally with ammonia. First, 3·5 g. of pure 3-*p*-nitrophenylpyridine were obtained, m. p. 148—149° alone or mixed with a specimen prepared (as above) from *p*-nitroaniline. Then a sticky precipitate was obtained, from which a further 0·1 g. of the above compound, m. p. 147—148°, was obtained by washing with ether and crystallising from alcohol, followed by an oil which was collected by ether. This, together with the residues from the mother-liquors of the 0·1 g. mentioned above, gave an oily residue (1·65 g.), which became mainly crystalline. Since no pure base could be isolated from it, it was converted into methosulphate and oxidised with permanganate; a mixture of acids not wholly nitrobenzoic acids was then obtained. The most sparingly soluble barium salt prepared from this mixture gave a trace of a crude acid, melting at about 130°, and at about 135° if mixed with *m*-nitrobenzoic acid. The total yield of the *p*-isomeride, 3·6 g., is 64·3% of the theoretical.

4-*Phenylpyridine and its Derivatives.*

4-p-*Nitrophenylpyridine* crystallises from acetone in nearly colourless, prismatic needles, m. p. 123—124° (corr.). It is insoluble in water, sparingly soluble in ether, and readily soluble in alcohol, acetone, or chloroform (Found: C, 65·9; H, 3·8; N, 14·0. $C_{11}H_8O_2N_2$ requires C, 66·0; H, 4·0; N, 14·0%). The *hydrochloride* crystallises from 5*N*-hydrochloric acid in nearly colourless, elongated prisms containing $3H_2O$, which are lost at 100°. The salt then has m. p. 255° (corr.) (Found, in air-dried salt: H_2O, 18·7. $C_{11}H_8O_2N_2,HCl,3H_2O$ requires $3H_2O$, 18·6%. Found in dried salt: C, 55·9; H, 4·1; Cl, 14·8. $C_{11}H_8O_2N_2,HCl$ requires C, 55·8; H, 3·8; Cl, 15·0%).

4-*p*-Nitrophenylpyridine was converted into 4-phenylpyridine through the amine and hydrazine, the same methods and proportions being used in each operation as in the case of the corresponding 2-isomerides, except that the 4-phenylpyridine was isolated in a different way, since it is scarcely volatile with steam. 4-p-*Aminophenylpyridine* was isolated as base in 89% yield. It crystallises from alcohol in large, well-formed, nearly colourless plates, m. p. 232—234° (corr.). It is insoluble in water, and sparingly soluble even in hot alcohol or ether. Consistent but low results were found on analysis (Found, in air-dried base: loss at 100°, 0·6. Found in dried base: C, 76·6, 76·5, 76·7; H, 5·7, 5·7, 5·9. $C_{11}H_{10}N_2$ requires C, 77·7; H, 5·9%). The *dihydrochloride* crystallises from dilute

hydrochloric acid in anhydrous, prismatic needles, m. p. 312° (decomp.; corr.) after darkening from about 240° (Found : Cl, 29·2. $C_{11}H_{10}N_2,2HCl$ requires Cl, 29·2%).

4-p-*Hydrazinophenylpyridine* is precipitated in an amorphous form on the addition of ammonia to an aqueous solution of its hydrochloride, but crystallises from alcohol in wedge-shaped bundles of nearly colourless needles, m. p. 205—207° (corr.). It is almost insoluble in water or ether and sparingly soluble in alcohol. The *dihydrochloride* crystallises from dilute hydrochloric acid in well-formed prisms, m. p. 272° (decomp.; corr.) (Found, in air-dried salt : loss at 100°, 6·6. $C_{11}H_{11}N_3,2HCl,H_2O$ requires H_2O, 6·5%. Found, in dried salt : Cl, 27·3. $C_{11}H_{11}N_3,2HCl$ requires Cl, 27·5%).

4-*Phenylpyridine* was prepared by oxidising the crude hydrazine with cupric acetate, removing copper by hydrogen sulphide, basifying the solution and collecting the product by ether, the yield being 24% of the theoretical calculated on the amine from which the hydrazine was prepared. After purification by distillation, conversion into the nitrate, and regeneration from the pure salt, it melted at 74° (corr.), alone or mixed with a specimen prepared by Hantzsch's general method. The preparation by this method has been described partly by Hantzsch (*Ber.*, 1884, **17**, 1512) and partly by Schiff and Piluti (*Ber.*, 1883, **16**, 1607). Since the latter authors especially give few details and the yield is not stated numerically in any of the various stages, the following supplementary information is given. Benzaldehyde (53 g.), ethyl acetoacetate (130 g.), aqueous ammonia (80 c.c., *d* 0·88), and alcohol (150 c.c.) were boiled under reflux, and after 2 hours another 20 c.c. of aqueous ammonia were added. After boiling for another 5 hours and keeping, the dihydro-ester (104 g.) was collected. The mother-liquor and alcoholic washings were mixed with another 20 c.c. of aqueous ammonia, boiled for 6 hours, and concentrated; more of the dihydro-ester then separated. The combined crops, after crystallisation from alcohol, gave ethyl 4-phenyl-2 : 6-dimethyl-1 : 4-dihydro-pyridine-3 : 5-dicarboxylate (120 g., yield 73%) in colourless prisms, m. p. 158—159° (corr.). Schiff and Piluti give m. p. 156—157°.

The dihydro-ester (104 g.), partly dissolved and partly suspended in ether (1 l.), was subjected to the action of nitrous acid, generated from a lower layer of aqueous sodium nitrite and sulphuric acid (the method of Rupe; compare Henle, "Anleitung für das organisch-chemische Praktikum," 1921, p. 180), until after 4 days no suspended matter remained and brown fumes were observed. The ethereal solution was washed with aqueous sodium carbonate, dried, and distilled, and the residue crystallised from alcohol; ethyl 4-phenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate was then obtained in

88·4% yield. It formed large, hexagonal plates, m. p. 62—63·5° (corr.), from alcohol. Schiff and Piluti give m. p. 66—67°.

This ester (30 g.) was heated with potassium hydroxide (15 g.) in absolute alcohol (45 c.c.), and the alcohol was then removed by distillation, eventually from an oil-bath at 130° and by adding water to the residue and again distilling. The product was oxidised in boiling aqueous solution by potassium permanganate (57 g.), an operation which took some 40 hours. Monopotassium 4-phenylpyridinetetracarboxylate was isolated by Hantzsch's method and recrystallised from water, 22 g. (yield 62%) being isolated in dense prisms. On concentrating the mother-liquors, needles separated and these were reoxidised with an equal weight of permanganate; a further quantity of the required salt was thus obtained in the characteristic dense prisms, the total yield being 72%.

On distilling this salt (161 g.) with lime and working up the product by Hantzsch's method, 41 g. of distilled 4-phenylpyridine were obtained. The yield in this operation was 61%, and the overall yield of this base from benzaldehyde was 28·3%. 4-Phenylpyridine distilled at 282—284° (corr.)/762 mm. (Hantzsch gives b. p. 274—275° uncorr.), but the base melts at 74° (corr.), not at 77—78° as stated by Hantzsch. The m. p. remained at 74° (corr.) both after the base had been crystallised from ether and after it had been converted into the nitrate and regenerated from the pure salt.

4-*Phenylpyridine dinitrate* crystallises from fairly concentrated nitric acid in colourless needles, m. p. 114—115° (corr.) (Found, in air-dried salt: C, 46·9; H, 4·2. $C_{11}H_9N,2HNO_3$ requires C, 47·0; H, 3·9%). When this salt is crystallised from absolute alcohol, 4-*phenylpyridine mononitrate* separates in colourless plates, m. p. 140° (corr.) (Found, in air-dried salt: C, 60·5; H, 5·0. $C_{11}H_9N,HNO_3$ requires C, 60·5; H, 4·6%). Both salts are easily soluble in water.

Nitration of 4-*Phenylpyridine.*—4-Phenylpyridine mononitrate (10 g.) was added to concentrated sulphuric acid (20 c.c.) cooled by water, and heated for ½ hour at 100°. The product was basified with ammonia, and the bases were collected partly by filtration and partly by extraction with ether. They were dissolved in hydrochloric acid (50 c.c. of 5*N*- + 10 c.c. of conc. acid); the hydrochloride of the *p*-nitro-derivative (4·35 g., m. p. 250°) then separated. The base regenerated from the mother-liquors was recrystallised from 5*N*-nitric acid (30 c.c.), the nitrate of the *m*-nitro-derivative (3·55 g., m. p. 215°) separating. The base from this mother-liquor was converted into hydrochloride, and gave another 1·2 g., m. p. 251°, of the *p*-salt. The further manipulation of the mother-liquors

consisted of fractional precipitation of the bases; the earlier fractions were crystallised as hydrochloride or nitrate (according to whether they were mainly *p* or *m*), and the later fractions were crystallised from 5*N*-nitric acid, yielding the well-crystallised nitrate of the *o*-isomeride. The three salts were then crystallised until pure from the appropriate 5*N*-acid, and the mother-liquors worked up by the above method. The final yields were 4-*p*-nitrophenylpyridine hydrochloride (+ $3H_2O$), 4·8 g. pure + 0·26 g., m. p. 246° (yield 38%); 4-*m*-nitrophenylpyridine nitrate, 3·37 g. pure + 0·07 g., m. p. 212° (yield 28·5%); and 4-*o*-nitrophenylpyridine nitrate, 1·53 g. pure (yield 12·7%).

The *p*-isomeride was identified as base and hydrochloride by comparison and by the mixed-m. p. method with 4-*p*-nitrophenylpyridine and its hydrochloride prepared (as above) from *p*-nitroaniline. 4-m-*Nitrophenylpyridine* crystallises from acetone in long, cream-coloured needles, m. p. 109—110° (corr.). It is insoluble in cold water, sparingly soluble in ether or hot water, but fairly easily soluble in alcohol or acetone (Found: C, 65·8; H, 3·9. $C_{11}H_8O_2N_2$ requires C, 66·0; H, 4·0%). The *nitrate* crystallises from 5*N*-nitric acid in anhydrous, cream-coloured needles, m. p. 222° (decomp.; corr.). (Found: C, 50·1; H, 3·4. $C_{11}H_8O_2N_2,HNO_3$ requires C, 50·2; H, 3·4%). It is very sparingly soluble in cold 5*N*-nitric acid. The orientation of the nitro-group was determined by heating 4-*m*-nitrophenylpyridine (0·5 g.) with methyl sulphate (0·5 c.c.) for 10 minutes at 100°, and oxidising the methosulphate in hot aqueous solution by permanganate; 0·12 g. of *m*-nitrobenzoic acid, m. p. 140—141° (alone or mixed with a known specimen), was thus obtained.

4-o-*Nitrophenylpyridine* crystallises from ether in colourless, elongated plates, m. p. 51—52° (corr.) to a turbid liquid, containing rather more than $1H_2O$. After drying in a vacuum over sulphuric acid, it retains $\frac{1}{2}H_2O$ (Found, in air-dried base: C, 59·7; H, 4·3; H_2O, 5·5. $C_{11}H_8O_2N_2,H_2O$ requires C, 60·5; H, 4·6; loss of $\frac{1}{2}H_2O$, 4·1%. Found, in dried base: C, 63·1; H, 4·2. $C_{11}H_8O_2N_2,\frac{1}{2}H_2O$ requires C, 63·2; H, 4·3%). The *nitrate* crystallises from 5*N*-nitric acid in large, nearly colourless, elongated prisms, m. p. 178—179° (corr.) (Found, in air-dried salt: loss at 100°, 2·1. Found in dried salt: C, 50·0; H, 3·4. $C_{11}H_8O_2N_2,HNO_3$ requires C, 50·2; H, 3·4%).

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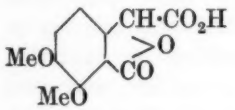
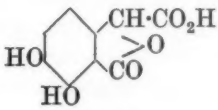
CCCLXXXIX.—*Synthesis of Some Derivatives of Methylenedioxybenzene.*

By William Henry Perkin, jun., and Victor Martin Trikojus.

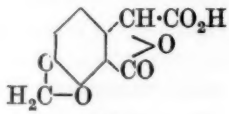
During the course of the experiments on the synthesis of cryptopine and protopine which have recently been brought to a successful conclusion (Haworth and Perkin, this vol., p. 1770), it seemed possible that the synthesis of oxy*epi*berberine—an essential step in the synthesis of cryptopine—might be achieved by employing methods similar to those which had been successful in the synthesis of oxyberberine (Perkin, Ray, and Robinson, J., 1925, **127**, 740). The remaining stages would then be (i) reduction to tetrahydro-*epi*berberine and (ii) the conversion of this substance into anhydrodihydrocryptopine followed by the oxidation of the latter to the amino-oxide by perbenzoic acid and treatment of this with acetic–hydrochloric acid (compare Haworth and Perkin, *loc. cit.*, p. 1773). In the synthesis of oxy*epi*berberine following the method of Perkin, Ray, and Robinson, the essential starting point is 3 : 4-*methylenedioxyphthalidecarboxylic acid* (III), and the present investigation was undertaken primarily with the object of preparing this important unknown acid. Starting with meconinecarboxylic acid (I), the idea was to convert this into 3 : 4-*dihydroxyphthalidecarboxylic acid* (II) by the action of hydriodic acid and then to introduce the methylene group by treating the acid or its ester with potassium hydroxide and methylene iodide.



(I.)



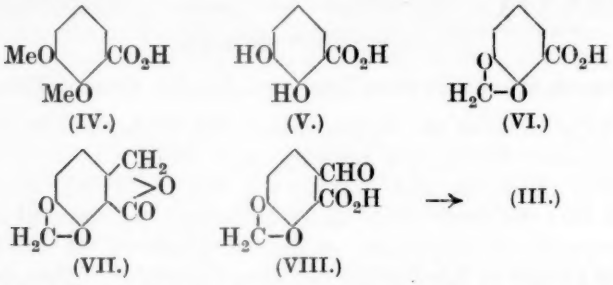
(II.)



(III.)

It was recognised at the time that the chance of success was a remote one and we were surprised to find that the acid (I), when treated with hydriodic acid under the conditions detailed on p. 2927, was converted without elimination of carbon dioxide quite smoothly into 3 : 4-dihydroxyphthalidecarboxylic acid (m. p. 215°), the intermediate stage being a monomethyl derivative (m. p. 203°), which is probably 3-*hydroxy*-4-*methoxyphthalidecarboxylic acid*. Unfortunately, however, in spite of a large number of experiments carried out under a variety of conditions, the final stage, namely, the conversion of (II) into (III), could not be accomplished, and therefore this route to the synthesis of cryptopine had to be abandoned.

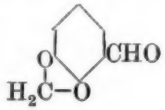
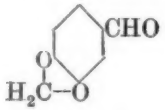
The next process we attempted will be clear from the following formula sketch :



o-Veratric acid (IV) is readily demethylated by heating with hydriodic acid and gives a good yield of 2 : 3-dihydroxybenzoic acid (*o*-protocatechuic acid, m. p. 204°), which had previously been obtained in small quantities by Miller (*Annalen*, 1883, **220**, 116, 126) by heating pyrocatechol with ammonium carbonate or by fusing 3-iodosalicylic acid with potassium hydroxide and recently by Kawai (*Sci. Papers Inst. Phys. Chem. Res.*, 3, 279—281, Tokio) in good yield by heating pyrocatechol with potassium carbonate and glycerol. This acid, now readily available, is converted (yield 45%) into 2 : 3-*methylenedioxybenzoic acid* (*o-piperonylic acid*, VI) when its solution in aqueous-alcoholic potassium hydroxide is vigorously stirred and heated with methylene iodide. *o*-Piperonylic acid condenses readily with formaldehyde in the presence of acetic–hydrochloric acid to yield 3 : 4-*methylenedioxyphthalide* (VII), a synthesis which, in view of the fact that ordinary piperonylic acid does not condense with formaldehyde under these conditions (Edwards, Perkin, and Stoyle, J., 1925, **127**, 196), was scarcely to be expected. Meconine (3 : 4-dimethoxyphthalide), on oxidation with manganese dioxide and sulphuric acid, is readily converted into opianic acid, and it therefore seemed probable that the analogously constituted 3 : 4-methylenedioxyphthalide (VII) would, without difficulty, yield the corresponding 3 : 4-methylenedioxyphthalaldehydic acid (VIII), from which it was hoped, by condensation with potassium cyanide followed by hydrolysis, to synthesise the substance (III). Unfortunately, however, the substance (VII) is so resistant to oxidation that no trace of the aldehydo-acid (VIII) could be isolated and therefore the process sketched above also had to be abandoned. The successful synthesis of oxy*epi*berberine and cryptopine by Haworth and Perkin (*loc. cit.*), using 3 : 4-methylenedioxy-2-carboxyphenylacetic acid instead of (III), has, in the meantime, rendered it unnecessary to continue the experiments on the synthesis of the acid (VIII).

The opportunity has been taken, during this investigation, to prepare and characterise several derivatives, such as the ethyl ester, amide and nitrile, of the hitherto undescribed *o*-piperonylic acid—an acid which, in many of its properties, resembles ordinary piperonylic acid.

2 : 3-*Methylenedioxybenzaldehyde* (*o-piperonal*, IX), the hitherto unknown isomeride of ordinary piperonal (X), was obtained by

(IX.)   (X.)

reducing *o*-piperonylonitrile with stannous chloride in the presence of an ethereal solution of hydrogen chloride according to the valuable method for the conversion of nitriles into aldehydes devised by Stephen (J., 1925, **127**, 1874). It melts at 34° and has an odour reminiscent of, but much fainter than, that of piperonal (m. p. 37°). Like piperonal, the oxime of which exists in two modifications (m. p. 112° and 146°), readily convertible into each other, *o*-piperonal gives at first an oxime, m. p. 127°, which, on standing, passes into the second modification, m. p. 138—139°, and when the latter is melted it reverts to the modification of m. p. 127°. *o*-Piperonal condenses readily with malonic acid to yield 2 : 3-*methylenedioxycinnamic acid*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO_2H$, m. p. 194°, and other derivatives of methylenedioxybenzene are described in the experimental part of this communication.

Experimental.

3 : 4-*Dihydroxyphthalidecarboxylic Acid* (*Normeconinecarboxylic Acid*, II).—Meconinecarboxylic acid (I; 20 g.) (Perkin, Ray, and Robinson, *loc. cit.*) was heated with five times its weight of freshly-distilled hydriodic acid (b. p. 126°), the temperature being gradually raised so as to permit of a uniform evolution of methyl iodide and being finally maintained at 130° for an hour; almost the theoretical quantity of methyl iodide collected in the receiver. After 12 hours, the crystalline acid was washed with a little very dilute sulphurous acid and crystallised from ethyl acetate–petroleum or from concentrated hydrochloric acid, separating in elongated prisms (13 g.), m. p. 215° with previous softening. A small quantity of cruder acid was obtained by concentrating the mother-liquor (Found: C, 51·1; H, 2·9. $C_9H_6O_6$ requires C, 51·4; H, 2·9%).

This acid is soluble in water, alcohol, or ethyl acetate and sparingly soluble in petroleum. The aqueous solution, which does not darken rapidly on addition of alkali, gives, with ferric chloride, an

intense green coloration which changes to crimson on the addition of sodium carbonate.

The *methyl* ester, obtained in the usual way by saturating a methyl-alcoholic solution of the acid with hydrogen chloride, crystallises from dilute methyl alcohol in needles. The air-dried substance melts at 104° and contains $1H_2O$ (Found: loss at 90°, 7·1. $C_{10}H_8O_6,H_2O$ requires H_2O, 7·4%). After drying at 100°, the methyl ester is anhydrous and melts at 150° (Found: C, 53·6; H, 3·9. $C_{10}H_8O_6$ requires C, 53·6; H, 3·6%). The substance is very soluble in alcohol and to some extent in water and the solution gives with ferric chloride a brilliant green colour changing to red on addition of sodium carbonate.

Attempts were made to methylenate normeconinecarboxylic acid under different conditions: (i) by using potassium hydroxide (3 mols.) and methylene iodide in aqueous alcohol; (ii) as (i), but using 4 mols. of potassium hydroxide so as to allow for the opening of the phthalide ring by hydrolysis; (iii) by heating the methyl ester in a sealed tube with potassium methoxide, methylene iodide, and methyl alcohol; (iv) as (iii), but substituting potassium amyloxide and amyl alcohol; (v) by heating the methyl ester in acetone solution with methylene iodide and anhydrous potassium carbonate. In each case the result was a negative one, but it is interesting that when pyrocatechol was employed under the conditions in (v) a 30—40% yield of pyrocatechol methylene ether resulted.

3-*Hydroxy*-4-*methoxyphthalidecarboxylic Acid*.—In a preliminary experiment on the demethylation of meconinecarboxylic acid the process was incomplete, since the product melted indefinitely at about 180°. Fractional crystallisation from ethyl acetate yielded as the less soluble portion an *acid* crystallising in colourless, glistening plates, m. p. 203° (Found: C, 53·6; H, 3·7. $C_{10}H_8O_6$ requires C, 53·6; H, 3·6%). It is appreciably soluble in water or alcohol and the solutions give with ferric chloride a blue coloration changed by sodium carbonate to brownish-pink.

2 : 3-*Dihydroxybenzoic Acid* (o-*Protocatechuic Acid*, V).—*o*-Vanillin (CHO : OH : OMe = 1 : 2 : 3) was converted into *o*-veratraldehyde by treatment, in methyl-alcoholic solution, with potassium hydroxide and methyl sulphate (compare the preparation of veratraldehyde from vanillin; Perkin and Robinson, J., 1907, **91**, 1079), and this was oxidised in hot dilute acetone solution with an equal weight of permanganate in 10% aqueous solution, sufficient acetone being added from time to time to keep the aldehyde in solution. After filtration, distillation of the acetone, and extraction with ether to remove traces of *o*-veratraldehyde, the alkaline solution was acidified; the precipitate, after being washed, was employed directly

for the demethylation. For this purpose, the acid (50 g.) was heated with freshly-distilled hydriodic acid (b. p. 126°; 300 g.) for about 2 hours, the temperature of the bath being finally raised to 135°. When the solution was cooled, *o*-protocatechuic acid rapidly separated; the crystals were collected after some time and washed with a little water. The dry, nearly pure, crystalline acid melted at 200° and was employed in this condition in the subsequent methylenation experiments. The hydriodic acid mother-liquor yielded, on evaporation, a small quantity of an acid which, after crystallisation from water, had a red tinge and contained iodine.

2 : 3-*Methylenedioxybenzoic Acid* (o-*Piperonylic Acid*, VI).—As the result of a number of comparative experiments, the following process was adopted for the preparation of this new acid. Finely-powdered *o*-protocatechuic acid (95 g.) was suspended in water (180 c.c.) in a flask fitted with a very rapidly working mechanical stirrer (closed by a mercury seal), an inlet tube for hydrogen, and a reflux condenser. After the air had been expelled by a stream of hydrogen, a solution of potassium hydroxide (103 g.) in water (400 c.c.) was added slowly, followed by methylene iodide (170 g.) dissolved in alcohol (250 c.c.). The whole was gently boiled by means of an oil-bath, with vigorous stirring to prevent the methylene iodide settling on the bottom of the flask and with continuous passage of hydrogen. The unchanged methylene iodide was then distilled in steam and the solution, after cooling in a stream of hydrogen, was acidified with concentrated hydrochloric acid. The crude o-*piperonylic acid* (65 g.), which separated as a light brown powder, was crystallised from alcohol, from which the acid separated in small, thick prisms (46 g.), m. p. 227°. A further quantity was obtained by working up the mother-liquor (Found: C, 58·1; H, 3·7. $C_8H_6O_4$ requires C, 57·8; H, 3·6%). The acid is very sparingly soluble in water but crystallises well from alcohol, ethyl acetate, or dilute acetic acid.

The *ethyl* ester, obtained by warming an alcoholic solution of the acid, saturated with hydrogen chloride, for a short time on the steam-bath, pouring the cooled mixture into sodium bicarbonate solution, and extracting this with ether, was a pleasant-smelling oil which distilled at about 272° and then crystallised in a freezing mixture. It separated from ether in elongated prisms, m. p. 35·5° (Found: C, 61·6; H, 5·4. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·1%).

2 : 3-*Methylenedioxybenzoyl chloride*. The acid (6 g.) was gently heated on the steam-bath for ½ hour with freshly-distilled thionyl chloride (18 c.c.). The excess of thionyl chloride having been distilled off, the acid chloride solidified and was sufficiently pure for conversion into the amide. It distilled readily under reduced

pressure and separated from benzene–petroleum in long, colourless needles, m. p. 116° (Found: Cl, 19·3. $C_8H_5O_3Cl$ requires Cl, 19·2%). When decomposed by water, it yielded *o*-piperonylic acid; this separated from alcohol in glistening, colourless prisms, whereas the acid prepared as described on p. 2929 is always brown, even after repeated crystallisation.

The *amide*, prepared by saturating a solution of the acid chloride in dry benzene with ammonia or by carefully pouring the benzene solution into excess of concentrated aqueous ammonia, separated from alcohol in colourless prisms, m. p. 176° (Found: C, 58·3; H, 4·4. $C_8H_7O_3N$ requires C, 58·2; H, 4·2%).

2 : 3-*Methylenedioxybenzonitrile* (*o-Piperonylonitrile*). The amide (4 g.) was heated on the steam-bath with thionyl chloride (20 c.c.) for 6 hours, and the product kept over-night. After the excess of thionyl chloride had been removed under reduced pressure, the substance remaining solidified when rubbed. Sodium carbonate was added until the product was neutral and the *nitrile*, obtained in almost quantitative yield, was washed with water and crystallised from dilute alcohol with the aid of animal charcoal (Found: C, 65·1; H, 3·6. $C_8H_5O_3N$ requires C, 65·3; H, 3·4%). This nitrile is readily soluble in alcohol, ether, or chloroform and separates in colourless needles, m. p. 80°. It is volatile in steam and the vapour has an odour reminiscent of that of benzonitrile.

2 : 3-*Methylenedioxybenzenylamino-oxime*,

$$CH_2O_2{:}C_6H_3{\cdot}C(NH_2){:}N{\cdot}OH.$$

The nitrile (0·5 g.) was warmed for about 12 hours with an alcoholic solution of hydroxylamine (from 0·36 g. of hydroxylamine hydrochloride and the equivalent quantity of sodium ethoxide), the alcohol removed, and the product mixed with ice; the *amino-oxime* then solidified. It separates from aqueous alcohol in colourless, flat prisms, m. p. 139°, and is soluble in acids and alkalis (Found: C, 53·6; H, 4·6. $C_8H_8O_3N_2$ requires C, 53·3; H, 4·4%).

3 : 4-*Methylenedioxyphthalide* (VII).*—*o*-Piperonylic acid (2 g.), dissolved in hot glacial acetic acid (10 c.c.), was mixed with concentrated hydrochloric acid (8 c.c.) and 40% formaldehyde (3 c.c.), and the mixture boiled for about ½ hour, until all had dissolved. The solution was diluted with water, mixed with excess of sodium bicarbonate, and extracted several times with chloroform. The solid (1 g.) remaining after the solvent had been dried and removed separated from glacial acetic acid in colourless, elongated prisms, m. p. 226°. These were sparingly soluble in hot water, but soluble in boiling dilute sodium hydroxide solution and were reprecipitated

* We are indebted to Dr. R. D. Haworth for carrying out this experiment.

by hydrochloric acid (Found: C, 60·5; H, 3·4. $C_9H_6O_4$ requires C, 60·7; H, 3·3%).

In attempts to convert this substance into 3 : 4-methylenedioxyphthalaldehydic acid, the following oxidising agents were tried without success, the meconine being either recovered unchanged or completely destroyed: (i) manganese dioxide and dilute sulphuric acid; (ii) as (i), but with the addition of glacial acetic acid to increase the solubility of the meconine; (iii) chromic anhydride and dilute sulphuric acid; (iv) potassium permanganate in acetone solution; (v) alkaline hydrogen peroxide.

2 : 3-*Methylenedioxybenzaldehyde* (o-*Piperonal*, IX).—Anhydrous stannous chloride (25 g.), prepared from the pyridine derivative by the method recommended by Stephen (J., 1925, **127**, 1874), was finely powdered, sieved, suspended in dry ether (150 c.c.), and saturated with dry hydrogen chloride until it had dissolved and the mixture had separated into two layers. *o*-Piperonylonitrile (8 g.), dissolved in chloroform (20 c.c.), was then added with rapid shaking in a flask fitted with a calcium chloride tube. A yellow solid soon began to separate and, after standing for 2 days with occasional shaking, this was collected and washed with chloroform. The solid, suspended in water, was heated for 3 hours on the steam-bath and the product was cooled and extracted several times with ether. The ethereal solution was concentrated and repeatedly extracted with aqueous sodium hydrogen sulphite, and the unchanged nitrile recovered by evaporating the ethereal solution. The aqueous extract was decomposed by sodium carbonate, the aldehyde extracted with ether, the ether evaporated, and the residue, which partly solidified, distilled in steam. The distillate deposited the solid aldehyde (2 g.), and a further quantity (0·6 g.) was obtained from the aqueous portion by extraction with ether. The substance crystallised from a very little alcohol or ether in colourless prisms, m. p. 34° (Found: C, 64·1; H, 4·1. $C_8H_6O_3$ requires C, 64·0; H, 4·0%).

The α- *and* β-*oximes.* When the aldehyde was rapidly treated with hydroxylamine hydrochloride and potassium carbonate in aqueous solution, and the product immediately crystallised from dilute methyl alcohol, the α-*oxime* was obtained in long, thin prisms, m. p. 127° (Found: C, 58·1; H, 4·4. $C_8H_7O_2N$ requires C, 58·2; H, 4·2%). When this oxime was kept, the melting point gradually rose to 138—139°, complete transformation into the β-modification having taken place. The β-*oxime* was obtained directly when the aldehyde was heated with hydroxylamine hydrochloride and potassium acetate for 2 hours (Found: C, 58·0; H, 4·5%). When the β-oxime was melted, it changed into the α-modi-

fication, the solidified mass melting at 127°. In time, however, the m. p. gradually rose to 138—139°.

The p-*nitrophenylhydrazone* separated immediately when the aldehyde, dissolved in acetic acid, was mixed with *p*-nitrophenylhydrazine in acetic acid and crystallised from acetic acid as a flocculent mass of minute, orange-red prisms, m. p. 258° (Found : N, 14·6. $C_{14}H_{11}O_4N_3$ requires N, 14·7%). Its colour is not so intensely scarlet as that of the corresponding derivative of ordinary piperonal.

2 : 3-*Methylenedioxycinnamic Acid*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO_2H$.—This acid was readily obtained when *o*-piperonal (0·22 g.), malonic acid (0·31 g.), pyridine (1·5 c.c.), and piperidine (2 drops) were heated on the steam-bath for 90 minutes, and the product poured into dilute hydrochloric acid. It is sparingly soluble in water and separates from dilute methyl alcohol or ethyl acetate in small, faintly yellow prisms, m. p. 194° (Found : C, 62·7 ; H, 4·3. $C_{10}H_8O_4$ requires C, 62·5 ; H, 4·2%). The corresponding dihydrocinnamic acid will be described in a future communication.

One of us (V. M. T.) is indebted to the Royal Commissioners of the 1851 Exhibition for a Studentship which has enabled him to take part in this investigation and also to the Research Fund Committee of the Chemical Society for a grant towards the expenses.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, September 20th*, 1926.]

CCCXC.—*The Density of Calcium Carbonate Hexahydrate.*

By JOHN HUME and BRYAN TOPLEY.

IN the course of experiments in dilatometers on the rate of decomposition of the unstable hexahydrate of calcium carbonate, it was observed that the increase in volume resulting from the complete decomposition of a known weight of hexahydrate did not correspond with the densities given in the literature for calcium carbonate and its hexahydrate.

The density of the calcite formed in the reaction was 2·72 (mean of nine experiments), which is also quoted as the best representative value by Mellor (" Treatise on Inorganic and Theoretical Chemistry," III, p. 835).

A review of the literature suggests that the properties of the hexahydrate may vary somewhat according to the conditions of preparation. The customary and most convenient method of

preparation is by precipitation with carbon dioxide from calcium oxide in sucrose solutions at 0°. The results below were obtained with crystals prepared in this way.

The density of the hexahydrate can be calculated from the expansion, measured in a dilatometer with a calibrated capillary tube, per g. of anhydrous calcium carbonate remaining. It is known, however, that calcium carbonate hexahydrate crystals tend to contain, as inclusions, small quantities of dyes and such salts as copper sulphate if they are present in the mother-liquor during growth (Kohlschütter and Egg, *Helv. Chim. Acta*, 1925, **8**, 697). It seems probable that crystals grown from 20% sucrose solutions would contain some sugar or its calcium derivative; indeed, if the very carefully washed crystals are allowed to decompose in contact with water, a residue is obtained on evaporation which chars on ignition, with a strong smell of burnt sugar, and leaves a residue of calcium carbonate. In order to allow for the effect (small in any case) produced by this included sugar or its calcium derivative upon the volume change in the dilatometer it has been assumed that the passage into solution of the included calcium derivative produces an increase in volume in the dilatometer, and that this increase can be calculated from the weight of the residue found on evaporation, on the assumption that the density of "calcium sucrate" solution is equal to that of a sucrose solution of the same concentration.

The density of the hexahydrate is then given by the expression :

$$D_{\text{Hexahydrate}} = \frac{D_{\text{Calcite}}\{208{\cdot}2 + (100{\cdot}1 \times 0{\cdot}00899)\}}{\{100{\cdot}1\,(1 - V\,.\,D_{\text{Calcite}}) + 108{\cdot}1\,D_{\text{Calcite}}\}}$$

where $D_{\text{Hexahydrate}}$ and D_{Calcite} represent the densities indicated by the suffix; V' = expansion actually observed (in c.c. per g. of calcite remaining); v = the correction already discussed; and $V = (V' - v)$.

The mean weight (five experiments) of "calcium sucrate" passing into solution per g. of calcite formed is 0·00899 g. Also, the corresponding expansion due to the different solubilities of the hydrated and the anhydrous forms would be about 0·0001 c.c. Taking this into consideration, v becomes 0·0039 c.c.

The following values for V' were obtained in nine dilatometer experiments : 0·313, 0·311, 0·323, 0·308, 0·319, 0·301, 0·310, 0·315, 0·316. For the density at 0° these figures give the respective values : 1·835, 1·832, 1·851, 1·827, 1·845, 1·816, 1·830, 1·838, 1·840. The mean of these is 1·834, and the average deviation from the mean 0·43%.

The density of the hexahydrate at 0° was determined also in the

following way. A specific gravity bulb was in turn filled, at 0°, with water, with the mother-liquor of the crystals, and with the mother-liquor together with some of the crystals, and weighed in each case. The object of this procedure is to avoid any contact of the crystals with pure water before the hexahydrate is weighed. In contact with 20% sucrose solution at 0°, the hexahydrate is stable for an indefinite time, but in contact with pure water decomposition proceeds slowly, even at 0°. The crystals were washed into a tared Gooch crucible, which was kept in water in a beaker; the beaker was warmed to complete the decomposition of the hexahydrate, and the calcite well washed. The crucible and its contents were dried and weighed. The washings were added to the liquid in which the Gooch had been standing; the whole was evaporated to dryness and the residue weighed. The weight of hexahydrate crystals is represented by the weight of calcite, calculated to $CaCO_3,6H_2O$, plus the weight of the residue. By this method the following values for the density were found: 1·828, 1·803, 1·803, 1·806, 1·833, 1·831, 1·812, 1·817. The mean of these is 1·817, the average deviation from the mean being 0·60%.

We are unable to account for the discrepancy of 0·9% between the values obtained by the two methods, but it is improbable that the average deviations of 0·60% and 0·43% respectively can be attributed wholly to experimental error. Factors affecting growth, such as the rate of absorption of carbon dioxide, and the extent to which the sugar has formed condensation products under the influence of the alkali, would seem to cause some variation in the density.

The value 1·817 is considerably higher than those given by other workers:

1·783/10°. Pelouze, *Compt. rend.*, 1865, **60**, 429.
1·752/18°. Bütschli, *Abh. Königl. Gesell. Wiss. Göttingen. Math. Phys. Kl.*, 1908, **6**, Nr. 31.
1·777/3°. Mackenzie, J., 1923, **123**, 2409.
1·789/15°. Hume, J., 1925, **127**, 1036.

Mackenzie's crystals were prepared in 10% sucrose solution; we have accordingly determined the density of crystals prepared from 10%, instead of 20%, sugar solution in both the ways described above; the density determined directly, at 0°, is 1·821, and that calculated from the expansion on decomposition is 1·833. Thus it does not seem possible to refer the difference between our value and Mackenzie's to the fact that the crystals were grown in sugar solutions of different concentrations.

THE UNIVERSITY, LEEDS. [*Received, July 28th*, 1926.]

CCCXCI.—*Solubility Influences. Part II. The Effect of Various Salts on the Solubility of Ethyl Acetate in Water.*

By Samuel Glasstone, Denys W. Dimond, and Edward C. Jones.

In Part I of this series (J., 1925, **127**, 2660), the influence of the alkali halides and of certain sugars on the solubility of ethyl acetate was described, and it was shown that when the added salt combined with or dissolved in the ethyl acetate the solubility measurements were of little value (compare Philip and Bramley, J., 1915, **107**, 377). In continuing these investigations, therefore, only substances which are almost insoluble in the ester have been used, *viz.*, sodium, potassium, and ammonium nitrates; ammonium acetate and oxalate; potassium fluoride, chlorate, and chromate; calcium, strontium, barium, and lead nitrates; barium and cupric chlorides; sodium, potassium, magnesium, nickel, copper, and zinc sulphates; and potassium ferro- and ferri-cyanides.

Experimental.

The experimental details were as described in Part I (*loc. cit.*). Whenever a salt was likely to interfere in any way with the estimation of the ethyl acetate in the solution, the sample taken for analysis was diluted and the ester distilled off. A portion of the saturated solution was always examined to make sure that the hydrolysis of the salt had caused no appreciable decomposition of the ester. All the solubility measurements were made at 25°.

The results have been calculated in exactly the same way as before; m and w represent the number of g.-mols. of added salt and of water, respectively, required to make a solution which will be saturated with 1 g.-mol. of ethyl acetate at 25°. The so-called "hydration number," n, which really gives a measure of the salting-out effect of 1 mol. of salt, is equal to $(w - w_0)/m$, where w_0, the value of w in pure water at 25°, is 66·15.

As before, the hydration numbers have been extrapolated to infinite dilution of the electrolyte; in some cases extrapolation is very uncertain, and so the values obtained are only approximate. The results of the extrapolation are given in brackets at the bottom of each "n" column.

The results recorded in the earlier paper indicate that the iodides either increase the solubility of ethyl acetate in water, or else reduce it to a small extent; it may be assumed, therefore, that the salting-out power of the iodine ion is negligible, and that it has a "hydration

Sodium nitrate.		
m.	*w.*	*n.*
0·29	67·3	3·8
0·82	74·9	10·6
1·86	79·2	7·0
5·58	105·9	7·1
14·25	157·0	6·4
27·25	219·3	5·6
		(15)

Lead nitrate.		
m.	*w.*	*n.*
0·072	65·9	—
0·20	71·1	24·5
0·49	81·2	30·6
1·04	78·4	11·7
1·92	82·9	8·7
		(38 ?)

Ammonium nitrate.		
m.	*w.*	*n.*
0·32	70·3	12·8
0·87	71·2	5·7
1·83	73·3	3·9
4·41	78·4	2·8
8·29	87·1	2·5
17·52	117·9	2·9
		(14)

Ammonium acetate.		
0·42	71·6	12·9
1·04	86·7	19·7
3·03	118·7	17·3
16·04	274·1	12·9
56·53	567·0	8·8
		(24)

Potassium chromate.		
0·14	71·7	39·3
0·42	86·4	48·1
1·25	124·0	46·2
6·70	288·6	33·2
56·16	1436·0	24·4
		(52)

Calcium nitrate.		
0·15	66·0	—
0·37	65·9	—
0·83	69·0	3·4
2·08	80·9	7·1
4·73	101·7	7·5
		(?)

Strontium nitrate.		
0·11	62·4	—
0·30	67·7	5·0
0·74	78·3	16·3
1·74	83·4	9·9
		(40 ?)

Barium nitrate.		
0·047	67·8	34·0
0·098	71·1	50·0
0·20	69·9	18·5
0·41	69·6	8·3
		(45 ?)

Potassium nitrate.		
0·25	68·7	10·0
0·68	72·8	9·7
1·51	76·8	7·0
3·69	83·0	4·6
		(13)

Barium chloride.		
0·051	66·7	9·8
0·10	68·1	19·0
0·31	75·6	30·3
0·73	89·7	32·2
1·19	91·6	21·4
3·36	136·8	21·0
		(50 ?)

Cupric chloride.		
0·078	73·0	87·8
0·15	72·9	45·0
0·29	76·0	33·9
0·45	83·3	38·1
0·76	89·0	30·0
1·14	99·4	30·0
		(110)

Nickel sulphate.		
0·094	73·0	72·3
0·27	80·1	51·5
0·68	100·4	50·3
2·13	147·4	38·1
6·62	281·2	32·5
17·73	531·5	26·2
		(90 ?)

Potassium sulphate.		
0·073	71·1	67·1
0·16	73·6	46·3
0·49	93·4	55·5
1·04	115·8	47·7
		(75)

Ammonium oxalate.		
0·097	74·3	83·5
0·20	79·6	67·0
0·35	88·0	62·3
0·52	98·9	62·9
		(85)

Magnesium sulphate.		
0·11	77·8	101·8
0·33	87·8	64·2
0·78	102·2	46·1
2·86	178·2	39·2
		(120)

Sodium sulphate.		
0·078	69·7	44·9
0·24	83·0	70·0
0·54	98·5	59·8
1·11	124·6	52·6
		(82)

Copper sulphate.		
0·11	78·1	108·2
0·30	81·2	50·0
0·78	102·7	46·8
1·59	132·7	41·8
		(150)

Zinc sulphate.		
0·089	71·0	54·0
0·27	83·1	62·6
0·68	103·4	54·7
2·01	142·2	37·8
		(72)

Potassium ferricyanide.		
0·077	72·0	75·3
0·22	77·1	49·5
0·53	87·8	40·8
1·44	106·4	27·9
3·34	145·5	23·7
		(105)

Potassium ferrocyanide.		
0·074	85·0	259·5
0·21	93·5	130·0
0·52	110·7	85·6
2·04	199·5	65·3
		(350)

Potassium chlorate.		
0·098	65·4	—
0·20	67·2	5·0
0·32	71·6	17·0
0·41	70·1	9·5
0·53	69·7	6·6
		(20 ?)

Potassium fluoride.		
0·53	80·4	26·8
1·95	119·4	27·3
8·83	258·3	21·7
		(29)

number " of zero. Combining this assumption with the results given here and in Part I, the " hydration numbers " *per equivalent* of various ions at infinite dilution may be readily deduced :

" Hydration " of Ions at Infinite Dilution.

Cations.						Anions.					
$Cu^{··}$	44	$Ni^{··}$	17	$NH_4^{·}$	11	$Fe(CN)_6^{''''}$	75	F'	17	ClO_3'	9
$Mg^{··}$	33	$Li^{·}$	17	$Rb^{·}$	10	C_2O_4''	31	CrO_4''	14	Br'	5
$Sr^{··}$	18 ?	$Na^{·}$	14	$Zn^{··}$	10	SO_4''	26	$C_2H_3O_2'$	13	NO_3'	2
$Ba^{··}$	17 ?	$K^{·}$	12	$Cs^{·}$	9	$Fe(CN)_6'''$	23	Cl'	10	I'	0
$Pb^{··}$	17										

These results indicate that in general the greater the valency of an ion the greater is the salting-out power of one equivalent. A large or complex ion, such as the ferricyanide ion, may, however, have only the same salting-out power as a smaller ion of lower valency.

Discussion.

It is generally accepted that a highly polar liquid will readily dissolve other polar liquids, but not those which are only slightly polar or non-polar (Hildebrand, " Solubility," 1924, p. 85); the greater the difference in polarity the less is the mutual solubility of the liquids. The molecules of water are highly polar and consequently in the liquid state they are held together in a strong electrostatic field; water is therefore said to be " associated." Such a liquid will naturally have a high cohesive power and a large internal pressure, and only a comparatively small solvent power for a non-polar substance like ethyl acetate. When a salt is added to the water the resultant ions will intensify the electrical field and so increase the polarity and the internal pressure (Hildebrand, *op. cit.*, pp. 97, 139; Lewis, *J. Amer. Chem. Soc.*, 1913, **35**, 1448; 1916, **38**, 762), with the result that the solvent power for a feebly polar substance is decreased. The more intense the electrical field produced by the ions of the added salt the greater should be the salting-out power of those ions. If we consider a series of univalent ions (*e.g.*, those of the alkali metals), the electrical field will be most intense in the vicinity of the smallest ion, *viz.*, the lithium ion, and hence the salting-out powers of the ions in the series should follow the order $Li > Na > K > Rb > Cs$. This order is in agreement with that actually found, and it should also hold good independently of the nature of the non-polar substance being salted out, provided that the salt does not combine with or dissolve in it. If the valency of the ion is increased the salting-out power per equivalent is generally increased too, and this suggests that owing to the concentration of several charges on one ion the electrical field per unit

charge is intensified; this appears to be quite reasonable. If the ion of higher valency is of large bulk, however, the effect of the increased number of charges may be counteracted; this seems to be the case with the ferricyanide ion.

The so-called " hydration number," which represents the magnitude of the salting-out power, is really a measure of the intensity of the electrostatic field surrounding an ion, on the basis of the views outlined above. If we adopt the physical interpretation of ionic hydration, according to which molecules are attracted electrostatically by the charged ion (Born, *Z. Elektrochem.*, 1920, **26**, 401; *Z. Physik*, 1920, **1**, 221; Debye and Hückel, *Physikal. Z.*, 1923, **24**, 305), then the number " n," although not representing stoicheiometrically the number of water molecules attached to each ion, is still a measure of what might be termed the " hydration effect."

The factors described above cannot, however, be the only ones at work in the process of salting-out. Apart from the difficulty of accounting simply for the " salting-out " power of the sugars (see Part I), we have to explain the abnormal results given by certain substances, *e.g.*, the nitrates. The hydration number of these salts, instead of decreasing with increasing concentration of salt, may be at first negative, then increase to a maximum, and finally decrease gradually. This suggests that two factors are at work; one, responsible for the salting-out effect, is opposed, particularly in dilute solution, by the second, which tends to increase the solubility of the neutral substance. Sugden (this vol., p. 174) has suggested that anions do not salt out at all, but exert to a varying extent a depolymerising effect on the associated water molecules, thus increasing their solvent power for a non-polar substance. A comparison of the salting-out powers of potassium nitrate and potassium ferrocyanide shows that this view is improbable, and that anions actually have a salting-out effect, although it is probably very small for the nitrate and iodine ions. An alternative suggestion is that the reduction of the dielectric constant of water in dilute solutions of electrolytes (Lattey, *Phil. Mag.*, 1921, **41**, 829; Ulich, *Z. Elektrochem.*, 1925, **31**, 413) may have some influence on the intensity of the electrical field in the liquid and so affect the power of dissolving neutral substances.

It is often suggested that there may be some connexion between the hydration of a salt in solution and its tendency to form stable solid hydrates. No such connexion could be detected when the hydration effect of sodium sulphate was determined both below and above the transition temperature between the decahydrate and the unhydrated salt, by measuring the solubility of ethyl acetate in a 7·5% solution of the salt. The results were as follows:

Temperature	10°	25°	38·5°	50°
Hydration number	47·6	54·4	52·0	53·0

These observations should have been made with a saturated solution of the salt, because it is from such a solution that the solid separates, but they show that it is very unlikely that the hydration effect is appreciably less at temperatures well above the transition point than it is below this temperature.

Summary.

(1) The solubility of ethyl acetate has been determined at 25° in solutions of a number of salts at various concentrations. The "hydration number" of each salt has been calculated and, where possible, extrapolated to give the value in a solution of infinite dilution.

(2) In general, the hydration effect of an ion is greater the greater its valency and the smaller its size.

(3) It is shown that the hydration of an ion and its salting-out power may both be due to the electrostatic field existing in the vicinity of the ion.

(4) The iodine and nitrate ions have a negligible salting-out power and frequently cause an increase in the solubility of neutral substances in water.

(5) The salting-out power of sodium sulphate in 7·5% solution appears to be the same below and above the transition temperature of the decahydrate.

UNIVERSITY COLLEGE, EXETER. [*Received, September 23rd,* 1926.]

CCCXCII.—*Solubility Influences. Part III. The Salting-out Effect of Mixtures on Aqueous Solutions of Ethyl Acetate.*

By SAMUEL GLASSTONE, DENYS W. DIMOND, and EDGAR R. HARRIS.

THE present investigation on the influence of a mixture of two substances on the solubility of ethyl acetate in water was undertaken not only with the object of contributing to the general problem, but also in order to study a possible method for the detection of complex-ion formation in solution. In the formation of a complex ion, in general, one molecule of undissociated salt and one or more simple ions are removed; hence it appeared possible that the salting-out power of the complex ion might differ appreciably from that of the constituents. By comparing the solubility influence of a mixture of salts which do not appreciably form complex ions (*e.g.*,

sodium and potassium chlorides) with the behaviour in a case in which complexes are probably formed (*e.g.*, potassium and cupric chlorides), it was hoped that some light would be thrown on this subject; the results obtained hitherto, however, have given no positive information.

The salting-out effects of the following mixtures, of varying composition, have been examined : Dextrose and sucrose, lævulose and sucrose, sucrose and sodium chloride, sodium and potassium chlorides, ammonium and sodium chlorides, ammonium and potassium chlorides, lithium and sodium chlorides, sodium and barium chlorides, potassium and cupric chlorides, and sodium and potassium nitrates. By a special method of calculation the salting-out effect of a mixture of substances is compared with the sum of the salting-out effects of the two constituents, making use of the results for single substances obtained previously (J., 1925, **127**, 2660; preceding paper).

Experimental.

The experimental method was exactly the same as that already described (*locc. cit.*). All the substances used had been examined earlier in these investigations. The solutions of the mixed substances were prepared by weighing the two separate amounts of the constituents and dissolving them in a known weight of water. The experimental temperature was 25·0° throughout. The columns headed M_1 and M_2 give the number of g.-mols. of each of the substances in the mixture in the order named at the head of each table of results, and w represents the number of g.-mols. of water required to make a solution which will just dissolve one g.-mol. of ethyl acetate at 25°. In pure water, the value of w, *i.e.*, w_0, is equal to 66·15, and $w - w_0$ is a measure of the salting-out power of the $M_1 + M_2$ g.-mols. of the two added substances; for convenience, the quantity $w - w_0$ is regarded as the number of g.-mols. of water " removed " or " fixed " by the mixture of substances. In order to compare the results obtained for the mixtures with those given by the separate constituents, the following method was adopted. From the results given in previous papers (*loc. cit.*), w was plotted against the concentration of added substance, m/w, for all the single substances involved in the present work. From the appropriate curves, the values of w_1 and w_2 corresponding to the concentrations M_1/w and M_2/w were read off; $w_1 - w_0$ and $w_2 - w_0$ then give the number of g.-mols. of water " fixed " by m_1 and m_2 g.-mols., respectively, of the two substances, where m_1/w_1 is equal to M_1/w, and m_2/w_2 to M_2/w. The number of g.-mols. of water " fixed " by M_1 and M_2 g.-mols., respectively, of the two added substances when each

is present in solution alone at the same concentration, relative to water, as it exists in the mixed solution will then be given by the expressions $(w_1 - w_0)M_1/m_1$ and $(w_2 - w_0)M_2/m_2$; these two quantities represent the separate salting-out effects of the two constituents of the mixture, and their sum, in the columns headed "$w - w_0$ calc." in Table I, is compared with the experimentally determined value.

TABLE I.

M_1.	M_2.	w.	$w - w_0$. (obs.)	$w - w_0$. (calc.)
Dextrose and sucrose.				
0·44	0·48	78·2	12·0	12·2
0·45	0·25	79·0	12·8	11·0
1·05	0·27	85·2	19·0	17·2
1·07	0·57	86·0	19·8	20·3
2·35	0·35	92·0	25·8	28·0
1·36	1·46	95·4	29·2	34·0
0·63	1·39	95·6	29·4	26·3
0·77	2·42	98·4	32·2	37·2
2·84	0·74	101·3	35·1	37·4
1·03	4·38	113·2	47·0	56·1
Sodium and potassium chlorides.				
2·08	0·77	118·0	51·8	53·4
1·77	1·60	119·5	53·3	62·0
3·34	0·83	123·3	57·1	75·4
2·95	4·58	160·0	93·8	116·9
Lævulose and sucrose.				
0·48	0·55	81·7	15·5	18·4
0·57	1·22	84·8	18·6	23·3
0·65	2·12	87·6	21·4	31·5
1·12	4·82	126·0	59·8	62·3
Sucrose and sodium chloride.				
0·27	1·69	104·2	38·0	34·7
0·62	1·85	110·0	43·8	38·5
1·42	1·93	118·1	51·9	50·5
2·88	2·02	128·6	62·4	67·4
2·16	2·11	131·7	65·5	60·1
0·41	4·74	146·0	79·8	79·7
0·85	5·03	153·6	87·4	86·1
0·43	7·90	169·2	103·0	108·4
2·80	8·36	187·4	121·2	143·9
0·97	29·8	333·8	267·6	307·6

The approximate agreement between the observed and calculated values of $w - w_0$ in the results quoted above indicates that for small concentrations the salting-out effect of a mixture of two substances, which do not form complexes, is almost equal to the sum of the separate effects; this is in agreement with the conclusions of Linde (*Arkiv Kemi, Min., Geol.*, 1917, **6**, No. 20, 1) who investigated the salting-out influence of mixtures of sodium sulphate and sulphuric acid (total conc., $N/2$), sodium sulphate and hydroxide (total conc., $N/2$), and sodium chloride and acetate (total conc., N) on an aqueous solution of ether. In more concentrated solutions, however, particularly when dealing with a mixture of two electrolytes, the salting-out influence is seen to be much less than would be expected if each salt exerted its own salting-out power at its particular concentration independent of the presence of the other. This is probably due to an electrical interaction between the two substances, and corresponds with the fact that the salting-out power per molecule of a single substance, in general, decreases with increasing concentration (see previous papers). In order to correct for the mutual interaction of the ions in the mixture, the calculations described above have been slightly altered; in determining the salting-out

power of each constituent of the mixture separately, it is assumed that its concentration is equal to the total concentration of the two salts, that is $(M_1 + M_2)/w$, instead of M_1/w or M_2/w. The values of w_1 and w_2 corresponding with this new concentration are then read off from the appropriate curves; from these m_1 and m_2 are determined, where m_1/w_1 and m_2/w_2 are each equal to $(M_1 + M_2)/w$. The number of g.-mols. of water " fixed " by each constituent is then given by the same expressions as used previously. By comparing the results thus obtained for mixtures of sodium and potassium chlorides with those given by the first method, it is seen that there is probably some justification for the assumption of mutual interaction of the ions of the substances in the mixture. The agreement between the observed and calculated values for the salting-out power, even in concentrated solutions, is noteworthy (Table II).

TABLE II.

M_1.	M_2.	w.	$w - w_0$. (obs.).	$w - w_0$. (calc.).
Sodium and potassium chlorides.				
2·08	0·77	118·0	51·8	47·8
1·77	1·60	119·5	53·3	52·6
3·34	0·83	123·3	57·1	63·7
2·95	4·58	160·0	93·8	96·2
7·47	2·70	190·0	123·8	126·9
16·34	4·36	274·2	208·0	214·6
5·57	17·63	274·7	208·5	219·2
13·55	11·12	308·6	242·4	254
36·68	7·16	448·6	382·4	387
Sodium and barium chlorides.				
0·71	0·16	84·3	18·1	19·0
0·92	0·38	93·6	27·4	28·9
0·83	0·60	97·2	31·0	34·6
1·74	0·21	104·9	38·7	37·8
0·88	0·83	105·9	39·7	43·0
3·19	0·25	123·9	57·7	59·5
Potassium and cupric chlorides.				
0·59	0·50	89·9	23·7	25·2
0·57	0·25	92·7	26·5	17·5 ?
1·27	0·27	96·0	29·8	30·9
0·68	0·85	99·0	32·8	36·7
0·73	1·22	104·2	38·0	47·3 ?
3·01	0·43	124·2	58·0	58·5
4·56	0·52	138·5	72·3	76·8

M_1.	M_2.	w.	$w - w_0$. (obs.).	$w - w_0$. (calc.).
Sodium and ammonium chlorides.				
0·92	0·86	96·3	30·1	29·2
1·98	1·07	116·2	50·0	44·8
Potassium and ammonium chlorides.				
0·59	0·83	91·7	25·5	23·9
1·37	0·93	102·1	35·9	35·0
Lithium and sodium chlorides.				
1·13	0·84	95·4	29·2	30·9
1·38	2·13	119·3	53·1	50·3
Sodium and potassium nitrates.				
0·39	0·34	70·6	4·4	7·5
0·43	0·76	76·3	10·1	8·8
0·46	1·27	77·7	11·5	12·2
0·47	1·64	79·4	13·2	14·6
0·94	0·80	80·5	14·3	13·0
1·46	0·47	82·9	16·7	13·3
1·13	1·91	91·3	25·1	16·5
7·39	1·55	131·9	65·7	53·1

The results obtained for other mixtures show that the salting-out power of a mixture is roughly equal to the sum of the salting-out powers of the constituents, provided allowance be made for the electrical interaction of the ions. In the case of the mixed nitrates, the results appear to be erratic; this is probably due to the fact that

these salts do not behave normally when salting-out ethyl acetate. A number of observations have also been made with mixtures of lead and sodium nitrates, lead and potassium nitrates, and lead and barium nitrates; owing to the same uncertainty, the detailed results are not given, but they tend to show, again, that the salting-out effect is additive.

The results obtained for the mixtures of potassium and cupric chlorides, in which complex-ion formation probably occurs, show that the salting-out property of ions cannot be utilised for the detection of complexes in solution. It has been shown (preceding paper) that an ion of high valency has, in general, a larger salting-out power per equivalent than one of lower valency. In the case under discussion, if the cuprichloride complex is bivalent then its salting-out power might be as great as the sum of the salting-out powers of the undissociated chloride and the two chlorine ions from which it is formed; the solubility influence of the mixture of potassium and cupric chlorides would then be the same as it would have been had no complex ion been formed. Although instances may subsequently be found in which abnormal solubility influences correspond with complex-ion formation, yet it is clear that normal results do not indicate an absence of such complexes.

The above results throw no light on the cause of the salting-out effect, because it is obvious that they may be explained equally well by the " hydration of ions " theory (Rothmund, *Z. physikal. Chem.*, 1900, **33**, 401) or by the " electrical stress " theory discussed in the preceding paper.

Summary.

(1) The influence of the following mixtures on the solubility of ethyl acetate in water at 25° has been investigated. Dextrose and sucrose, lævulose and sucrose, sucrose and sodium chloride, sodium and potassium chlorides, sodium and ammonium chlorides, potassium and ammonium chlorides, lithium and sodium chlorides, barium and sodium chlorides, potassium and cupric chlorides, and sodium and potassium nitrates.

(2) The salting-out power of a mixture is, in general, equal to the sum of the salting-out powers of the constituents, provided allowance be made for the electrical interaction of ions.

(3) The salting-out effect cannot be utilised for the detection of complex-ion formation.

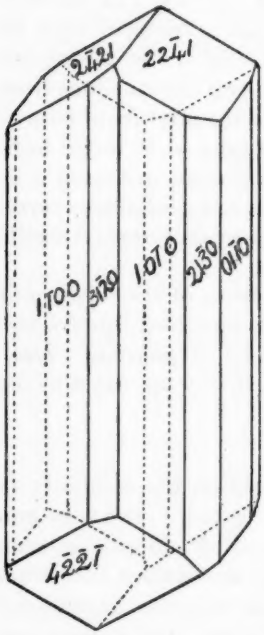
UNIVERSITY COLLEGE, EXETER. [*Received, September 23rd*, 1926.]

CCCXCIII.—*The Crystal Structure of Quinol. Part I.*

By William Augustus Caspari.

Quinol is the only disubstituted benzene derivative except guaiacol known to crystallise in trigonal or hexagonal symmetry. Its most stable modification crystallises from water with highly acicular habit, in hexagonal prisms capped by rhombohedra. The crystals used in the present investigation (Fig. 1) were prepared by slow evaporation, at room temperature, of aqueous solutions to which a little potassium bisulphite had been added. Prisms of all thicknesses up to 1·5 mm. were thus obtained; the prism faces in many cases showed longitudinal striations, whilst the rhombohedra usually had smooth polished faces and sharp edges.

Fig. 1.



Heydrich (*Z. Kryst. Min.*, 1910, **48**, 244) placed quinol in the ditrigonal-scalenohedral or calcite class. Re-examination by the goniometer, however, showed that the hexagonal prism edges are frequently blunted by narrow faces of a third-order prism, which in some individuals may be identified on all six edges. The mean prism-zone angle between first and third orders was 40° 58′ (calc. for $10\bar{1}0 : 12\bar{3}0$, 40° 54′). The crystal must therefore be placed in the trigonal-rhombohedral or dioptase class, space-group C^1_{3i} or C^2_{3i}. Laue photographs through the (0001) plane (which, however, was never observed as a crystal face) showed trigonal symmetry. Through the $(10\bar{1}0)$ and $(11\bar{2}0)$ planes, the latter of which, again, does not occur on the crystal, they showed no symmetry. The evidence of Laue photographs therefore confirms the above conclusion.

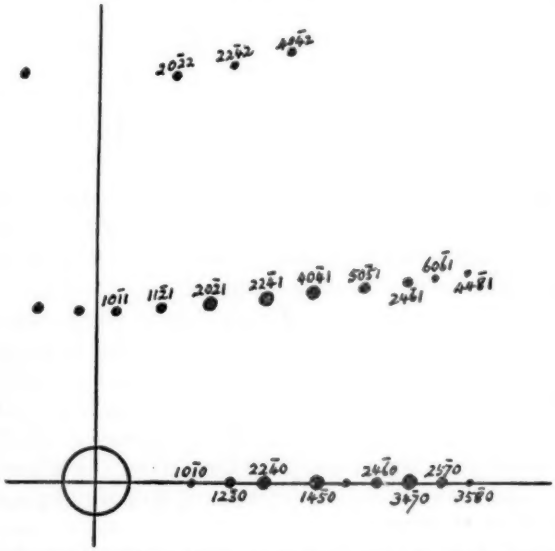
Interpenetration-twinning between right and left third-order prisms is common, and some care was needed in selecting untwinned crystals suitable for *X*-ray photography.

The crystal structure of quinol has been examined by Becker and Jancke (*Z. physikal. Chem.*, 1921, **99**, 242), whose results are somewhat at variance with those given below. These investigators,

however, used only the powder method, which is now known to be of minor utility for the determination of unit cells.

Crystals of the requisite quality having been secured, *X*-ray rotation photographs were taken with axes of rotation normal to the planes (0001), (11$\bar{2}$0), and (10$\bar{1}$0), respectively. A quarter of the first-named, or *c*-axis, diagram is shown in Fig. 2, the intensities of the reflexion-spots being roughly indicated by their size. From measurements of eight spots lying on two layer-lines, the cell-dimension along this axis is found to be $c = 5{\cdot}62$ Å. The first

FIG. 2.



Quinol, rotated about c*-axis, as for* 8·0 *cm. distance. Cu* K_α *radiation.*

layer-line is rather more intense than the centre-line and much more so than the second layer-line. From this it is inferred that there is no interleaving plane of molecules normal to the *c*-axis. Oscillation photographs from the (0001) plane confirmed this conclusion: they showed a strong first-order (0001) line and (0002) and (0003) lines of diminishing intensity.

The closeness of the spots along the first layer-line in Fig. 2 indicates a long *a*-dimension of the cell; as will be seen below, its actual value is 22·08 Å. For a hexagonal crystal, the general equation for the distances of (*hkl*) planes from an origin (compare Hull, *Physical Rev.*, 1917, **10**, 661) reduces to

$$1/d^2 = 4(h^2 + k^2 + hk)/3a^2 + l^2/c^2,$$

or, for the present case,

$$1/d^2 = 0{\cdot}00274(h^2 + k^2 + hk) + 0{\cdot}0317l^2,$$

by means of which equation indices may be assigned to the spots as follows:

	d (obs.).	d (calc.).		d (obs.).	d (calc.).
$10\bar{1}0$	9·48	9·55	$10\bar{1}1$	5·47	5·39
$12\bar{3}0$	7·19	7·22	$11\bar{2}1$	5·11	5·01
$12\bar{4}0$	5·48	5·50	$20\bar{2}1$	4·75	4·84
$14\bar{5}0$	4·27	4·16	$22\bar{4}1$	4·03	3·94
$24\bar{6}0$	3·61	3·61	$40\bar{4}1$	3·60	3·60
$34\bar{7}0$	3·14	3·13	$50\bar{5}1$	3·16	3·15
2570	3·01	3·06	$24\bar{6}1$	2·94	3·03
$35\bar{8}0$	2·71	2·72	$60\bar{6}1$	2·72	2·76
			$44\bar{8}1$	2·51	2·47

	d (obs.).	d (calc.).
$20\bar{2}2$	2·63	2·69
$22\bar{4}2$	2·55	2·51
$40\bar{4}2$	2·40	2·42

The rotation photographs normal to $(11\bar{2}0)$ and $(10\bar{1}0)$ determined the cell-dimension along a satisfactorily. The former, showing seven layer-lines, gave $a = 22{\cdot}06$ Å.; the latter, with thirteen layer-lines, gave $a\sqrt{3} = 38{\cdot}23$ Å., whence $a = 22{\cdot}08$ Å.

Both these photographs showed layer-lines of fairly even intensity, well filled with reflexion-spots. Those from the main prism presented some interest: $(10\bar{1}0)$ was absent, whilst (2020), (4040), and $(60\bar{6}0)$ occurred as strong spots; $(50\bar{5}0)$ was found only in one photograph. Taking into account the weakness of $(10\bar{1}0)$ on the c-axis photograph, we may conclude that there is a partial halving of $(10\bar{1}0)$; *i.e.*, these planes are interleaved half-way by a somewhat similar layer of molecules.

Oscillation-photographs from the main prism face showed five or more orders giving $d_{10\bar{1}0} = 19{\cdot}1$ Å. This agrees with the cell-dimension $a = 22{\cdot}1$ Å. if $d_{10\bar{1}0} = a\sqrt{3}/2$. It follows that the unit cell of quinol is hexagonal, not rhombohedral. That this is the case may indeed be expected from the acicular habit of the crystal, which points to much closer packing of molecules upon the prism faces than upon any pyramidal face. The space-group of the crystal is therefore C_{3i}^{1}.

On calculating the number of molecules of quinol (sp. gr. 1·33) in the cell, we find

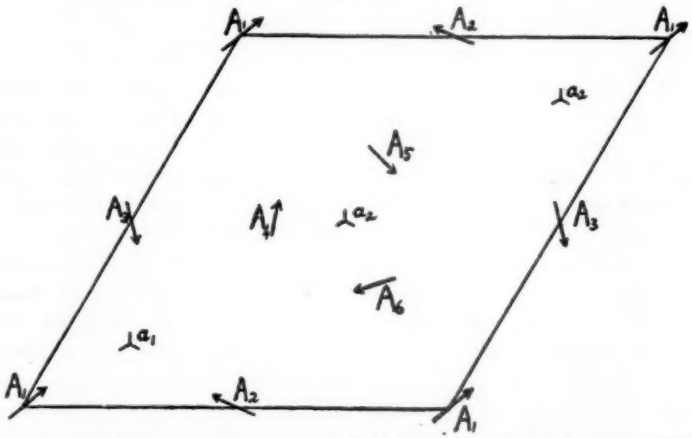
$$n = \frac{5{\cdot}62 \times (22{\cdot}07)^2 \times \sqrt{3}/2 \times 1{\cdot}33}{110 \times 1{\cdot}65} = 17{\cdot}4.$$

Hence there are 18 molecules to the cell. The space-group, however, requires only 6 asymmetric molecules as a maximum, and

we must infer that the lattice-units consist, not of single molecules, but of groups of three forming an asymmetric whole.

The disposition of lattice-units must be approximately as in Fig. 3, which represents a projection of the cell upon the (0001) plane. We have seen above that this plane repeats itself at 5·62 Å. intervals without interleavings. Lattice-units A_1, A_2, and A_3 are grouped around the triad axis a_1. So also, but with different orientation, are A_4, A_5, and A_6. Groupings around the secondary triad axes a_2 follow automatically. All the lattice-units are placed as far from one another as possible, since the space actually taken up by the molecules does not leave much room for gaps. A_2 and

FIG. 3.



Quinol, projection of unit cell upon (0001) *plane. The rhombus has sides of* 22·08 *Å. length and is* 5·62 *Å. distant from the next in the plane of the paper. Each* A *represents a group of three molecules.*

A_3 lie half-way between A_1, in accordance with the partial halving of $(10\bar{1}0)$. A_6 lies on a line between A_1 and A_3, coinciding with the developed face $(12\bar{3}0)$. An arrangement of the atoms cannot be attempted at present, since there is nothing to indicate how the molecules are triply associated into lattice-units.

This association of molecules found in the quinol crystal appears to have no connexion with the familiar molecular association in the liquid or gas phase. Quinol, according to Auwers (*Z. physikal. Chem.*, 1895, **18**, 595), is not associated at all in naphthalene solution, and is actually less so than pyrocatechol and resorcinol, which are unassociated in the crystal. Crystal-phase association was first observed in sulphur; a recently discovered organic example is fumaric acid (Yardley, J., 1925, **127**, 2207, where other examples

are cited). From unpublished results worked out by, or communicated to, the author it would appear that association of two molecules occurs in several other organic crystals, and the phenomenon may indeed be a somewhat common one.

The author desires to thank Sir William Bragg, F.R.S., for the interest he has taken in this work and for his valuable suggestions.

DAVY FARADAY LABORATORY,
ROYAL INSTITUTION. [*Received, June 5th,* 1926.]

CCCXCIV.—*The Spectra of the Phosphorescent Flames of Carbon Disulphide and Ether.*

By HARRY JULIUS EMELÉUS.

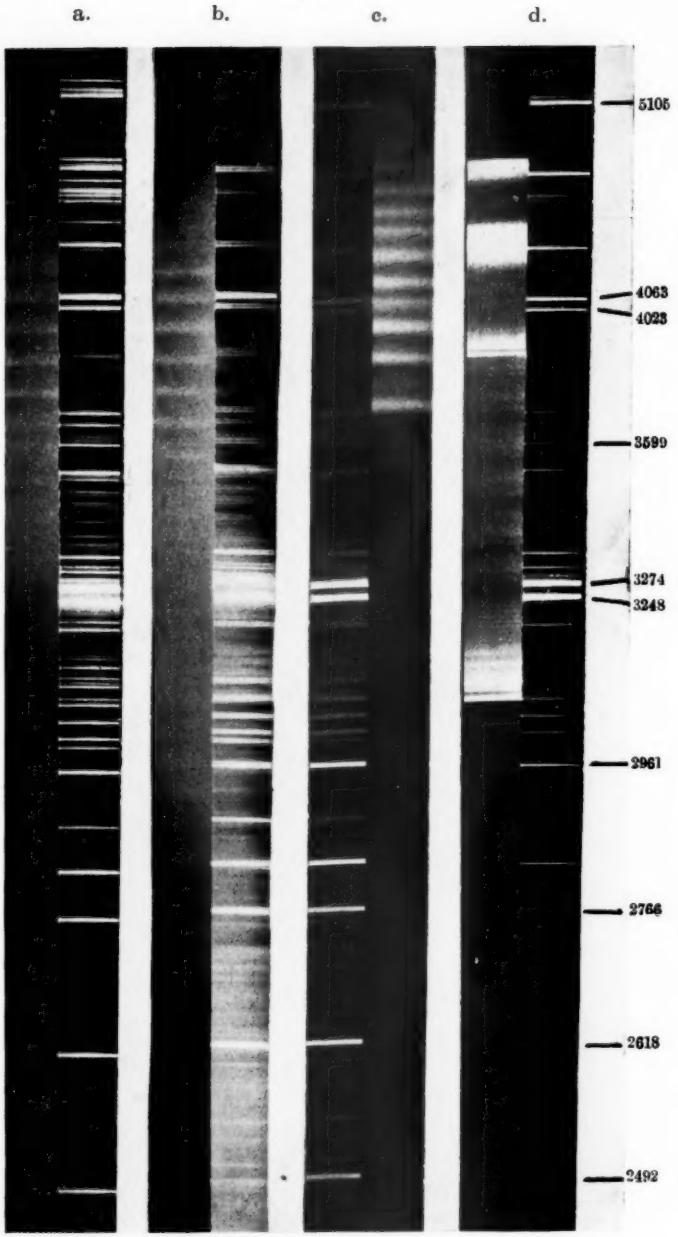
WHEN a combustible mixture containing carbon disulphide or ether is maintained at a temperature somewhat below the ignition point, a feebly luminous and relatively cool flame is produced, which is termed the *phosphorescent flame* by analogy with the well-known glow of phosphorus. This mode of combustion of ether was studied by Perkin (J., 1882, **41**, 363), who found that little carbon dioxide was formed and that aldehydes could be isolated. The phosphorescent flame of carbon disulphide was investigated by Dixon and Russell (J., 1899, **75**, 600) and by Dixon (*Rec. trav. chim.*, 1925, **44**, 305), and the partial nature of the oxidation was again demonstrated by the isolation of carbon monosulphide. The spectra of these flames have now been studied and compared with those of the substances burning normally.

A Hilger quartz spectrograph (size E. 6), for the loan of which the author is indebted to the Air Ministry, was used. Although this instrument has a small dispersion for wave-lengths greater than 3000 Å.U., it is rapid in action, and therefore well suited for the very feeble light sources examined.

Spectra of the Phosphorescent and Normal Flames of Carbon Disulphide.

Carbon disulphide was purified by distillation from paraffin wax and stored in contact with mercury. A transparent silica tube (15 cm. long and 1·4 cm. internal diameter), open at both ends, was heated electrically over the upper 5 cm. of its length by a winding of resistance wire; it was clamped vertically with the heated zone opposite the slit of the spectrograph, and a slow stream of nitrogen saturated with carbon disulphide was passed upwards through it from a jet. By adjusting the heating current the phosphorescent

FIG. 1.



a. *Carbon disulphide, normal flame spectrum—8 seconds.* b. *Carbon disulphide, phosphorescent flame spectrum—80 hours.* c. *Ether, phosphorescent flame spectrum—180 hours.* d. *Ether, normal flame spectrum—8 hours. Copper-arc reference spectra.*

[*To face p.* 2948.]

flame was produced, its temperature varying between 180° and 250°. Exposures of 40—250 hours were made on rapid plates, a copper-arc reference spectrum being superposed in every case. Photographs of the normal flame spectrum were obtained by burning nitrogen saturated with the vapour at a jet in an atmosphere enriched with oxygen.

The phosphorescent flame gave a band spectrum which shows certain differences from that of the normal flame. The bands were degraded towards the red, extending from 4530—3400 Å.U., and from 3100—2480 Å.U. Between these two groups the spectrum appeared to be continuous. The violet edges * of the bands in the first group were measured in the usual way. Those of shorter wave-length were measured by superposing an accurately divided scale on an enlargement, the latter values being checked on the negative by a wave-length scale. In Table I, the wave-length of the violet edge and the estimated relative intensity of each band are given; it is considered that the maximum error in the observations is 10 Å.U. above 3000 Å.U., and 5 Å.U. below.

TABLE I.

Wave-lengths of the violet edges of bands in the spectrum of the phosphorescent flame of carbon disulphide.

λ.	λ.	λ.	λ.	λ.	λ.
4530 (3)	4040 (8)	3550 (5)	2910 (4)	2765 (2)	2605 (2)
4440 (4)	3940 (10)	3500 (5)	2890 (1)	2730 (5)	2590 (3)
4350 (4)	3830 (7)	3410 (4)	2865 (5)	2715 (2)	2575 (3)
4310 (1)	3730 (7)	3100 (5)	2850 (2)	2700 (4)	2540 (2)
4250 (5)	3680 (2)	3045 (5)	2820 (5)	2680 (1)	2510 (1)
4190 (2)	3640 (6)	2995 (5)	2800 (2)	2655 (4)	2485 (1)
4150 (8)	3590 (5)	2955 (5)	2780 (4)	2620 (2)	

The spectrum of the normal carbon disulphide flame has been only incompletely described, perhaps owing to the heavy continuous background (compare Kayser, "Handbüch d. Spectroscopie," Vol. 6), but the present measurements establish its identity with that of the phosphorescent flame between 4530—3400 Å.U. A group of closely-spaced bands occurring between 3400—2900 Å.U. was not observed in the low-temperature flame. These, however, may have become merged in the continuous background. The bands below 3100 Å.U. were much less intense in the hot flame than in the glow, as illustrated by photographs *a* and *b* (Fig. 1). The former is a short exposure (8 secs.) of the normal flame spectrum, no bands being visible below 3400 Å.U. In the latter, which is an

* The violet edges are utilised in these measurements, both because they are sharp and because they are probably very close to the head of the band.

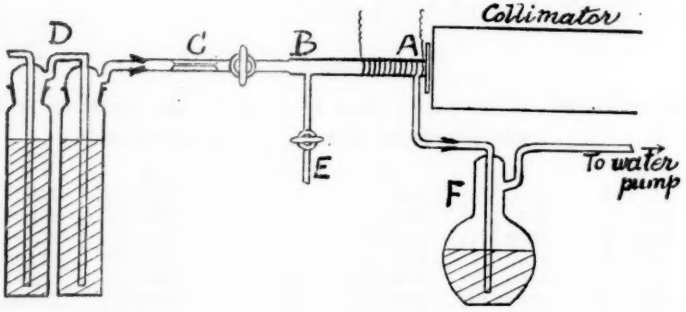
80-hour exposure of the phosphorescent flame spectrum, the group between 3100—2480 Å.U. is very little less intense than that above 3400 Å.U. A similar intensity variation was observed in the flame spectra of phosphorus and some of its compounds under various conditions (Emeléus, J., 1925, **127**, 1362).

Spectra of the Normal and Phosphorescent Flames of Ether.

Ether (B.P., pure for anæsthesia) was used without further treatment. The apparatus for producing the phosphorescent flame is shown in Fig. 2.

The tube AB (3·5 mm. internal diameter) had a quartz window cemented to the ground end A, and was heated electrically over a distance of 5 cm. from it by an external winding of resistance wire. The bubblers, *D*, containing ether, and the wash bottle, *F*, containing water, were connected by ground joints, no lubricant being used

FIG. 2.



either on these or on the taps. The capillary, *C*, was inserted to prevent the passage of a flame back into *D*. A stream of air saturated with ether vapour was drawn through the heated tube, the temperature of which was adjusted so that a phosphorescent flame resulted. Its brightness was increased on admitting a slow stream of air at *E*. By arranging *AB* in alinement with the collimator slit, satisfactory negatives were obtained in 180—250 hours, a moderately wide slit and rapid plates being used. The spectrum of the blue zone at the base of the normal hot ether flame was also photographed.

The phosphorescent ether flame gave a band spectrum, of which (*c*) is an enlargement (180 hours' exposure). The violet edges of the bands, which were degraded towards the red, were measured, the wave-lengths and estimated relative intensities being given in Table II. Owing to the indefinite nature of the edge, and the low dispersion, an error of 5—10 Å.U. may occur in certain cases.

TABLE II.

Wave-lengths of the violet edges of bands in the spectrum of the phosphorescent ether flame.

λ.	λ.	λ.	λ.	λ.
4930 (1)	4550 (7)	4210 (8)	3940 (9)	3670 (8)
4785 (3)	4425 (7)	4115 (8)	3840 (8)	3520 (4)
4675 (5)	4345 (7)	4040 (5)	3745 (3)	3385 (2)

Examination of the corresponding wave-numbers shows the existence of nearly constant differences, indicating that this spectrum has a normal structure. Certain of the heads correspond with sulphur bands, but no sulphur could be detected analytically, nor were the bands in question observed with long exposures of the normal ether flame. Since the spectra differ in general appearance, the coincidence was regarded as fortuitous.

The light from the low-temperature ether flame gives a totally different spectrum from that of the ordinary flame, of which (*d*) is an enlargement (8 hours' exposure). The latter is the well-known hydrocarbon flame spectrum, showing the " water bands " and the " Swan bands " prominently. It is concluded that the incomplete combustion (compare Perkin, *loc. cit.*) is the cause of the different light emission. No previous description of this spectrum can be traced.

The author wishes to thank Professor H. B. Baker, F.R.S., in whose laboratory these experiments were carried out, for his interest and advice. He is also indebted to Professor A. Fowler, F.R.S., for his advice and assistance in examining the spectra. The commencement of this work was made possible by a maintenance grant from the Department of Scientific and Industrial Research, and it has been completed during the tenure of an 1851 Senior Studentship. Part of the apparatus was purchased from a grant by Messrs. Brunner Mond and Co., Ltd.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, July 29th,* 1926.]

CCCXCV.—*Aminobenzthiazoles. Part V. Stability of the* 1-*Alkylaminobenzthiazole Bromides.*

By ROBERT FERGUS HUNTER.

RECENTLY, as the fourth object of this investigation (see footnote, this vol., p. 1385), the study of the relation between unsaturation and mobility in triad systems of the aminothiazole type was commenced. Since the tautomerism of 1-aminobenzthiazole with the

corresponding 1-imino-1 : 2-dihydro-derivative had already been established (*loc. cit.*), the 1-alkylaminobenzthiazole system appeared to be suitable for the examination of the effect of diminishing mobility of the hydrogen atom [H] on the unsaturation of the nitrogen atom of the thiazole nucleus.

On the basis of Ingold's modified strain theory (J., 1921, **119**, 305, 951; Deshapande and Thorpe, J., 1922, **121**, 1432; compare also Bains and Thorpe, J., 1923, **123**, 1206; Lanfear and Thorpe, *ibid.*, p. 2865) it seems probable that increasing the atomic volume of the alkyl group R in the 1-alkylaminobenzthiazole system (I $\rightleftharpoons$ II) would increase the stability of the two-membered, heterocyclic ring, N=C, of the aminothiazole phase (I) and thus would enhance this phase of the tautomeric system (compare Packer and Thorpe, this vol., p. 1203). Consequently, on ascending the homologous series of 1-alkylaminobenzthiazoles, a gradual shift of the equilibrium in favour of the phase (I) is to be expected.

(I.) $C_6H_4\langle\overset{S}{N}\rangle C\cdot NHR \rightleftharpoons C_6H_4\langle\overset{S}{N[H]}\rangle C{:}NR$ (II.)

The nuclear nitrogen atom of the aminothiazole phase (I) has more residual affinity than the corresponding nitrogen atom of the iminodihydro-phase (II), since it has free affinity due to the nuclear double bond in addition to its own residual affinity. The nuclear nitrogen atom in the phase (I) is, then, more unsaturated than that in the phase (II) and hence, on increasing the bulk of the alkyl group R, a corresponding increase in the unsaturation of the thiazole nucleus should ensue, leading to an increase in the stability of the bromo-addition compound of the alkylaminothiazole. Experiments on the stability of the bromides of 1-alkylaminobenzthiazoles (R = Me up to *n*-heptyl) have therefore been made with the view of testing this point and obtaining some knowledge of the effect on the carbon tetrahedral angle of the hitherto unstudied butyl, amyl, and hexyl groups (Hunter, footnote, this vol., p. 1401).

The bromo-addition compounds of the 1-alkylaminobenzthiazoles obtained from the corresponding *s*-phenylalkylthiocarbamides were first examined. In view of the remarkable instability of 1-aminobenzthiazole dibromide, which rapidly loses bromine on exposure to the atmosphere (*loc. cit.*), it seemed that the stability of the bromides could be most conveniently tested by measuring the decrease in labile bromine content produced by exposing them to air under similar conditions. Unfortunately, owing to the tendency of the thiazole nucleus in the 1-alkylaminobenzthiazoles to add on more than two bromine atoms, the difficulties attending the iodometric estimation of the labile bromine (due to a part of the labile

bromine entering the benzene nucleus, giving rise to bromo-substitution derivatives), and to the physical properties of the compounds, a stability curve could not be obtained. Greater success, however, has attended the study of the 5-bromo-1-alkylaminobenzthiazole system, and experiments are described in the following paper which confirm the view here suggested regarding the increase in unsaturation of the nuclear nitrogen atom produced by an increase in the volume of R.

With the exception of the *n*-propyl compound, all the *s*-phenylalkylthiocarbamides, on bromination in chloroform, readily passed either into the *dibromides* (III) of the corresponding 1-alkylaminobenzthiazoles or into the *hydrobromides* of these (IV or V). Thus

(III.) $C_6H_4\langle{}^{S\text{---}}_{NBr_2}\rangle C\cdot NHR$ $\quad$ $C_6H_4\langle{}^{S\text{---}}_{NBr_2}\rangle C\cdot NHR,HBr$ (IV.)

(V.) $C_6H_4\langle{}^{S\text{---------}}_{NBr_2(HBr)}\rangle C\cdot NHR$ $\quad$ $C_6H_4\langle{}^{SBr_2}_{NBr_2}\rangle C\cdot NHPr^{\alpha}$ (VI.)

s-phenylethylthiocarbamide readily yielded the *dibromide* of 1-ethylaminobenzthiazole (III, R = Et), a bright red compound of the usual type which gradually lost bromine on exposure to air, liberated iodine from dilute hydriodic acid, yielded a bromo-substitution derivative on treatment with dilute alcohol, and was reduced to 1-ethylaminobenzthiazole (I or II, R = Et) by sulphurous acid and sulphur dioxide in the usual way (*loc. cit.*). Similarly, *s*-phenyl-*n*-butylthiocarbamide and *s*-phenyl-*n*-hexylthiocarbamide gave the *dibromides* of 1-*n*-butylamino- and 1-*n*-hexylamino-benzthiazoles (III, R = n-C_4H_9 and n-C_6H_{13}, respectively). On the other hand, *s*-phenyl*iso*butylthiocarbamide, *s*-phenyl-*n*-amylthiocarbamide, and *s*-phenyl-*n*-heptylthiocarbamide yielded *tribromo*-addition compounds of 1-*iso*butylamino-, 1-*n*-amylamino-, and 1-*n*-heptylamino-benzthiazoles (IV or V, R = *iso*-C_4H_9, n-C_5H_{11}, and n-C_7H_{15}, respectively) similar to the tribromide of 5-methyl-1-aminobenzthiazole (this vol., p. 1389).

s-Phenyl*iso*amylthiocarbamide yielded the *tribromo*-addition compound of 1-*iso*amylaminobenzthiazole, a compound of the usual type which could not be obtained crystalline. This difficulty was experienced with 5-bromo-1-*iso*amylaminobenzthiazole tribromide also (Hunter and Soyka, following paper) and appears to be associated with the *iso*amylamino-group.

s-Phenyl-*n*-propylthiocarbamide gave a red *tetrabromide* of 1-*n*-propylaminobenzthiazole (VI) which, on exposure to air, rapidly lost bromine with the formation of a yellow, stable *dibromide*. Both bromides had the usual properties and gave 1-*n*-propylaminobenzthiazole on treatment with sulphurous acid.

By bromination under the conditions described in this paper, *s*-phenylmethylthiocarbamide has been converted directly into the stable yellow dibromide of 1-methylaminobenzthiazole previously obtained from the unstable tetrabromide (this vol., p. 1393). This dibromide, which is remarkably stable in moist air, resembles the stable tribromides of the 1-arylaminobenzthiazoles (J., 1925, **127**, 2025) and is quite distinct from the red dibromo-addition compounds of 1-ethylamino- and 1-*n*-butylamino-benzthiazoles. Since it is formed from the unstable tetrabromide by exposure to air, it may be produced by loss of bromine across the heterocyclic nucleus of (VI, with Me in place of Pr^{n}) and may contain the :S:Br·NBr complex. This suggestion applies also to the stable yellow dibromide of 1-*n*-propylaminobenzthiazole.

The results of the experiments on the stability of the 1-alkylaminobenzthiazole bromides are tabulated below.

Alkyl group.	Bromide.	Labile halogen (initial) %.	Labile halogen (final) %.	Exposure in hours.
Methyl.	Dibromide.	24·8	24·4	46
Ethyl.	,,	45·4	30·4	44
n-Propyl.	Tetrabromide.	51·3	27·7	,,
n-Butyl.	Dibromide.	32·8	32·6	,,
*iso*Butyl.	Tribromide.	32·3	17·9	48

Experimental.

1-*Methylaminobenzthiazole Dibromide.*—A solution of *s*-phenylmethylthiocarbamide (1 g.) in chloroform (6 c.c.) was slowly treated with bromine (0·8 c.c.) and heated under reflux for 2—5 minutes; hydrogen bromide was then copiously evolved. On slight concentration, cooling and scratching, the dibromide separated in small, yellow crystals, which were collected on porous earthenware and dried in a vacuum over potassium hydroxide. They turned brownish-orange at 105—106°, crumbled slightly at about 120°, and sintered and decomposed at 144—146° (Found: Br, 50·5. Calc. for $C_8H_8N_2Br_2S$: Br, 49·4%). The compound was reduced by sulphurous acid to 1-methylaminobenzthiazole (this vol., p. 1394) and liberated iodine from dilute hydriodic acid. After exposure to air at 17°/770 mm. for 46 hours, it sintered and decomposed at 134—137°, but the labile bromine content was almost unaltered (see table).

1-*Ethylaminobenzthiazole dibromide* was obtained in a similar way from 2 g. of *s*-phenylethylthiocarbamide (Weith, *Ber.*, 1875, **8**, 1524) in chloroform (10 c.c.) and bromine (1·5 c.c.), a labile dibromo-addition compound of the thiocarbamide (?) (compare Hugershoff, *Ber.*, 1903, **36**, 3121) being precipitated and redissolving before the solution was heated. The red gum obtained solidified in glistening,

red needles, which were dried in a vacuum over potassium hydroxide; m. p. 76—78° (decomp.) (Found: Br, 47·2. $C_9H_{10}N_2Br_2S$ requires Br, 47·3%). This compound has the usual properties of the dibromides. After 44 hours' exposure to air, it melted at 48°, becoming red and soft at 40—45°, and the labile bromine content decreased by 15%.

1-*Ethylaminobenzthiazole* was obtained by treating the dibromide, suspended in sulphurous acid, with sulphur dioxide, and the filtered solution with ammonia (*d* 0·880). It crystallised from alcohol in small, glistening prisms, m. p. 87—88° (Found: S, 18·1. $C_9H_{10}N_2S$ requires S, 17·9%).

1-n-*Propylaminobenzthiazole Tetrabromide.*—*s*-Phenyl-*n*-propylthiocarbamide (Hecht, *Ber.*, 1890, **23**, 286) (1·5 g.) in chloroform (6 c.c.) was slowly treated with bromine (0·9 c.c.) and the mixture was refluxed for 2 minutes, concentrated, and cooled; a red gum separated slowly which could not be crystallised. This was dissolved in chloroform containing bromine, and the solution evaporated slowly in a vacuum; the *tetrabromide* then crystallised in small, vermilion prisms which melted at 54—56° (decomp.) after being dried in the usual way (Found: Br, 63·1. $C_{10}H_{12}N_2Br_4S$ requires Br, 62·5%). The compound lost bromine appreciably in ½ hour, and after 44 hours' exposure, it was yellowish-orange and melted at 65°, softening at 59—61°.

1-n-*Propylaminobenzthiazole dibromide* was obtained in small, orange prisms by exposing a thin layer of the tetrabromide to air for 5 days. After being washed with ether and dried in a vacuum, it melted at 80—82° (decomp.) (Found: Br, 47·5. $C_{10}H_{12}N_2Br_2S$ requires Br, 45·7%).

1-n-*Propylaminobenzthiazole* was obtained from either of the preceding bromides in the usual way and separated from alcohol in small prisms, m. p. 68° (Found: S, 17·0. $C_{10}H_{12}N_2S$ requires S, 16·7%).

s-*Phenyl*-n-*butylthiocarbamide.*—*n*-Butylamine (2 g.) was condensed with phenylthiocarbimide (4 g.) in alcohol in the usual way. The *thiocarbamide*, after being washed with light petroleum (b. p. 40—60°), was obtained in shining, flat prisms, m. p. 65° (Found: S, 15·4. $C_{11}H_{16}N_2S$ requires S, 15·4%).

1-n-*Butylaminobenzthiazole Dibromide.*—When phenyl-*n*-butylthiocarbamide (2 g.) in chloroform (8 c.c.) was slowly treated with 1·3 c.c. of bromine a violent reaction took place, the solution boiling spontaneously with evolution of hydrogen bromide. The mixture was refluxed, concentrated, and cooled in a freezing mixture; the *dibromide* then suddenly crystallised in small, glistening, orange prisms which, after drying, became soft and red at 80° and melted

at 86° (decomp.) (Found: Br, 42·4. $C_{11}H_{14}N_2Br_2S$ requires Br, 43·7%). The compound had the usual properties. After 44 hours' exposure to air, it became soft and red at 79—80° and melted at 82—84°, but the labile bromine content was almost unaltered. After several weeks' exposure, however, it lost bromine and became almost colourless.

1-n-*Butylaminobenzthiazole*, obtained from the dibromide, on recrystallisation from alcohol separated in small, glistening plates, m. p. 87° (Found: S, 15·8. $C_{11}H_{14}N_2S$ requires S, 15·5%).

1-iso*Butylaminobenzthiazole Dibromide Hydrobromide*.—*s*-Phenyl-*iso*butylthiocarbamide (Hecht, *Ber.*, 1892, **25**, 813; Dixon, J., 1893, **63**, 320) was treated like the *n*-butyl compound. Cooling having failed to induce crystallisation, the solution was treated with bromine–chloroform, and the solvent removed in a vacuum. The red gum obtained, after being kept in a vacuum over potassium hydroxide for 18 hours, changed to small, orange-red prisms on being rubbed. These were very soluble in chloroform and were resinified by ether or petroleum, and therefore they were crushed and again dried in a vacuum. The substance became red at about 50°, softened at 60°, and melted at 66—68° (decomp.) (Found: Br, 52·5. $C_{11}H_{14}N_2Br_2S,HBr$ requires Br, 53·7%). After 48 hours' exposure to air, it melted at 50° and the labile bromine content decreased by more than 14%.

1-iso*Butylaminobenzthiazole* separated from alcohol in small, shining needles, m. p. 103—104° (Found: S, 15·6. $C_{11}H_{14}N_2S$ requires S, 15·5%).

s-*Phenyl*-n-*amylthiocarbamide* was obtained from *n*-amylamine and phenylthiocarbimide in the usual way and crystallised from alcohol in glistening plates, m. p. 69—71° (Found: S, 14·2. $C_{12}H_{18}N_2S$ requires S, 14·5%).

1-n-*Amylaminobenzthiazole Dibromide Hydrobromide*.—A solution of phenyl-*n*-amylthiocarbamide (1 g.) in chloroform (6 c.c.) was slowly treated with 0·7 c.c. of bromine, heated under reflux, and concentrated in a vacuum over potassium hydroxide. The *tribromide* was thus obtained in small, vermilion-orange crystals, m. p. 90° (decomp.; reddening at 60°) (Found: Br, 52·6. $C_{12}H_{16}N_2Br_2S,HBr$ requires Br, 52·4%).

1-n-*Amylaminobenzthiazole* crystallised from alcohol in rosettes of glistening needles, m. p. 68—69° (Found: S, 14·2. $C_{12}H_{16}N_2S$ requires S, 14·6%).

1-iso*Amylaminobenzthiazole Dibromide Hydrobromide*.—Treatment of phenyl*iso*amylthiocarbamide (Dixon, J., 1893, **63**, 324) (1·5 g.) in the usual way (chloroform, 6 c.c.; bromine, 1 c.c.) produced a red gum. This was freed from solvent in a vacuum and agitated

with a current of air; the orange-red resin thus obtained would not crystallise (Found: Br, 47·8. $C_{12}H_{16}N_2Br_2S$,HBr requires Br, 52·4%).

1-iso*Amylaminobenzthiazole*, prepared from the bromide in the usual way, crystallised from alcohol in aggregates of needles, m. p. 69—71° (Found: S, 14·7. $C_{12}H_{16}N_2S$ requires S, 14·6%).

s-*Phenyl*-n-*hexylthiocarbamide* was obtained from *n*-hexylamine and phenylthiocarbimide in the usual way and crystallised from alcohol in small prisms, m. p. 103—104° (Found: S, 13·5. $C_{13}H_{20}N_2S$ requires S, 13·6%).

1-n-*Hexylaminobenzthiazole Dibromide*.—This was prepared from *s*-phenyl-*n*-hexylthiocarbamide (0·5 g.), chloroform (5 c.c.), and bromine (0·5 c.c.). The crude product, a red gum, after being kept in a vacuum over potassium hydroxide for 24 hours, changed to orange prisms of the *dibromide*, m. p. 100—102° (decomp.; sintering at 90°) (Found: Br, 41·2. $C_{13}H_{18}N_2Br_2S$ requires Br, 40·6%).

1-*n*-*Hexylaminobenzthiazole*, prepared from the dibromide in the usual way, crystallised from alcohol in small, glistening prisms, m. p. 57° (Found: S, 13·8. $C_{13}H_{18}N_2S$ requires S, 13·7%).

s-*Phenyl*-n-*heptylthiocarbamide*, prepared from *n*-heptylamine and phenylthiocarbimide in alcohol, crystallised from this solvent in small prisms, m. p. 70—71° (Found: S, 13·0. $C_{14}H_{22}N_2S$ requires S, 12·8%).

1-n-*Heptylaminobenzthiazole Dibromide Hydrobromide*.—A solution of phenyl-*n*-heptylthiocarbamide (1·5 g.) in chloroform (8 c.c.) was treated with bromine (0·9 c.c.), refluxed for 3 minutes, and concentrated in a vacuum; the *tribromide* then crystallised in small, orange-yellow, glistening prisms, m. p. 79—81° (after drying) (Found: Br, 48·2. $C_{14}H_{20}N_2Br_2S$,HBr requires Br, 49·1%).

1-n-*Heptylaminobenzthiazole* was prepared by keeping the tribromide in contact with sulphurous acid for a week and boiling the product with 10% sodium hydroxide solution. The colourless oil obtained solidified in glistening plates on cooling and then crystallised from alcohol in shining needles, m. p. 55° (Found: S, 13·0. $C_{14}H_{20}N_2S$ requires S, 12·9%).

In view of the trypanocidal activity of 1-aminobenzthiazole the chemotherapy of its alkyl derivatives will be examined.

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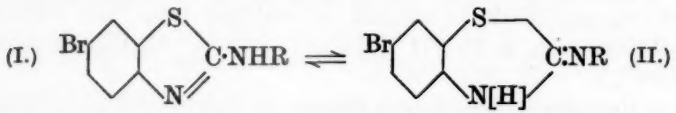
CCCXCVI.—*Aminobenzthiazoles. Part VI. The Addition of Bromine to Nascent Tautomeric Systems of the Aminothiazole Type and the Mobility and Unsaturation of the 5-Bromo-1-alkylaminobenzthiazole System.*

By Robert Fergus Hunter and Charles Soyka.

Of the two main experimental difficulties in determining the stability of the 1-alkylaminobenzthiazole bromides (preceding paper, p. 2952), that due to migration of bromine into the benzene nucleus can usually be prevented by introducing a bromine atom into this nucleus in the para-position to the reactive nitrogen atom (Fries, *Ber.*, 1904, **37**, 2388; *Annalen*, 1906, **346**, 128). In view of this and because the mobility of 5-bromo-1-aminobenzthiazole had already been established by the symmetry test (Hunter, this vol., p. 1389), it was decided to examine the mobility and unsaturation of the 5-bromo-1-alkylaminobenzthiazole system (I ⇌ II). The



choice of this system was a fortunate one, for the presence of the 5-bromo-substituent removed both difficulties referred to above and it was possible to isolate a series of dibromides of the required type and examine their stability. The physical properties of the 5-bromo-1-alkylaminobenzthiazole dibromides, however, made it impossible to extend the investigation beyond the *iso*butyl homologue.

The 5-bromo-1-alkylaminobenzthiazole bromides were obtained by brominating the corresponding *s*-*p*-bromophenylalkylthiocarbamides in chloroform (compare Hunter, J., 1925, **127**, 2023). These reacted much more slowly than the unbrominated thiocarbamides, owing to the effect of the substituent bromine and possibly also to the tendency to form the thiazole bromide (Hunter, *loc. cit.*).

The transformation of arylthiocarbamides into 1-aminobenzthiazole bromides doubtless occurs as follows : Bromine is added on at the double bond of the C:S group of the thiocarbamide, giving rise to an unstable dibromo-compound containing the CBr·SBr group; this then loses hydrogen bromide, and the nascent benzthiazole formed (Hugershoff, *Ber.*, 1903, **36**, 3121; compare also Hofmann, *Ber.*, 1880, **13**, 11) adds on bromine, giving the thiazole bromide

(Hunter, *loc. cit.*). This addition takes place in a mobile triad system, and from the 5-bromo-1-alkylaminobenzthiazole system either or both of the dibromides (III) and (IV) might be produced.

(III.) $C_6H_3Br<^{S\text{——}}_{NBr_2}>C{\cdot}NHR$ $\qquad$ $C_6H_3Br<^{S\text{——}}_{N[H]Br_2}>C{:}NR$ (IV.)

It is noteworthy that two forms of 2-β-naphthylamino-α-naphthathiazole have been isolated from the product of brominating *s*-di-β-naphthylthiocarbamide in chloroform under very slightly different conditions (J., 1925, **127**, 2271) and similar observations have been made on the tribromide of 1-amino-5-methylbenzthiazole (this vol., p. 1389).

By brominating *s*-ethyl-, *s*-*n*-propyl-, *s*-*n*-butyl-, and *s*-*iso*butyl-*p*-bromophenylthiocarbamides in chloroform under similar conditions, the dibromides of the corresponding 5-bromo-1-alkylaminobenzthiazoles were obtained. These were all coloured, crystalline compounds of the usual type which decomposed at the melting point and were reduced by sulphurous acid to the corresponding 5-bromo-1-alkylaminothiazoles; they displayed, however, somewhat unusual stability to moist air.

The dibromides differed considerably from one another in initial velocity of reduction by dilute hydriodic acid under similar conditions: 5-bromo-1-ethylaminobenzthiazole dibromide was quantitatively reduced, whereas reduction of the *iso*butyl homologue did not exceed 20% As the table shows, the stability of the compounds was in the expected order—ethyl<*n*-propyl<*n*-butyl<*iso*butyl—and thus the view expressed in the preceding paper is confirmed with regard to the effect of increasing atomic volume of the alkyl group on the unsaturation of the nuclear nitrogen atom.

Stability of the 5-Bromo-1-alkylaminobenzthiazole Dibromides.

Alkyl group.	% Bromine liberated.	% Labile bromine reacting.
Ethyl	38·0	98·9
n-Propyl	17·7	42·4
n-Butyl	15·1	37·3
*iso*Butyl	7·7	19·0

The great difference in stability between the *n*-butyl and the *iso*butyl compounds illustrates the very large effect produced by the *iso*butyl group, which is somewhat similar to a *gem*-dialkyl group (Ingold, J., 1921, **119**, 305, 951).

The bromination of *s*-*p*-bromophenylethylthiocarbamide under different conditions gave even more interesting results. When the labile 5-bromo-1-ethylaminobenzthiazole dibromide was boiled for some time with a mixture of bromine and chloroform, it was converted into an *isomeride* having the same chemical but different

physical properties and resembling 5-bromo-1-*iso*butylaminobenzthiazole dibromide in stability towards hydriodic acid. Both dibromides gave 5-bromo-1-ethylaminobenzthiazole on reduction with sulphurous acid, and therefore it appears highly probable that they are the dibromides (III and IV) of the tautomeric forms of 5-bromo-1-ethylaminobenzthiazole, the labile derivative (IV, R = Et) being formed from the iminodihydro-phase of the mobile triad system. Its conversion into the stable bromide appears, then, to involve merely a transference of the potentially mobile hydrogen atom and the necessary shifting of the double bond, and suggests the possibility of retarded mobility (Kon and Linstead, J., 1925, **127**, 813) between the bromides involving quinquevalent nitrogen—a possibility which the authors hope to investigate at a future time.

The percentage reductions of the 5-bromo-1-alkylaminobenzthiazole dibromides recorded in the table on p. 2959 are not a measure of the equilibrium of the symmetrical triad system, but, since the brominations and the reductions were both carried out under similar conditions, they do definitely indicate the shift of equilibrium in favour of the more unsaturated aminothiazole phase. The dibromides of *n*-propyl-, *n*-butyl-, and *iso*butyl-amino-5-bromobenzthiazoles probably contain appreciable quantities of the isomeric dibromides. The melting point is unfortunately no criterion of purity, because the compounds decompose rapidly on fusing (compare Reade, J., 1924, **125**, 150).

Bromination of 5-bromo-1-ethylaminobenzthiazole (as distinct from the nascent thiazole formed in the bromination of bromophenylethylthiocarbamide) yielded a bromide, m. p. 204° (decomp.), apparently consisting almost entirely of the labile dibromide obtained from the iminodihydro-form (II) of the base.

s-p-Bromophenylmethylthiocarbamide behaved abnormally on bromination, giving rise to the ***hexabromide*** of 5-bromo-1-methylaminobenzthiazole (V), one of the stablest of these hexabromides as yet isolated. Bromination of *s-p*-bromophenyl-*n*-amylthiocarbamide produced the *tetrabromide* of 5-bromo-1-*n*-amylaminobenzthiazole (VI), a difficultly crystallisable substance of the usual type.

$C_6H_3Br\langle^{SBr_4}_{NBr_2}\rangle C{\cdot}NHMe$ (V.) $C_6H_3Br\langle^{SBr_2}_{NBr_2}\rangle C{\cdot}NH{\cdot}C_5H_{11}$ (VI.)

s-n-Hexyl-, *s-n*-heptyl-, and *s-iso*amyl-*p*-bromophenylthiocarbamides on bromination all gave rise to the corresponding 5-bromo-1-alkylaminobenzthiazole dibromides (III) or (IV). The difficulty of crystallising these prevented examination of their

quantitative reduction by hydriodic acid. They are compounds of the usual type and give the corresponding 5-bromo-1-alkylaminobenzthiazoles on reduction.

EXPERIMENTAL.

s-Di-*p*-bromophenylthiocarbamide was best prepared in quantity as follows: A solution of *p*-bromoaniline (500 g.) in a mixture of carbon disulphide (700 c.c.) and alcohol (600 c.c.) containing a little sulphur (compare Hugershoff, *Ber.*, 1899, **32**, 2245) was kept for several weeks; a large quantity of the dithiocarbamate then crystallised. A mixture (800 c.c.) of alcohol and carbon disulphide (4 : 1) was then added, and the whole refluxed for 3 hours. On cooling, the thiocarbamide crystallised in long, hard, shining needles, m. p. 184—185°. A further quantity was obtained by concentrating the mother-liquor. Yield, 480 g. (86%).

p-Bromophenylthiocarbimide was prepared by boiling a solution of *s*-di-*p*-bromophenylthiocarbamide (100 g.) in acetic anhydride (120 c.c.) (compare Werner, J., 1891, **59**, 396) for 15 minutes, pouring it into water (200 c.c.) at 60—80°, and steam-distilling the product. Yield, 40 g.; m. p. 60—61°.

The thiocarbamides described below were prepared by heating *p*-bromophenylthiocarbimide and the requisite amine in alcoholic solution and either crystallising the product from alcohol or extracting it with small quantities of ether until the m. p. was constant.

s-p-*Bromophenylmethylthiocarbamide* crystallises in shining needles, m. p. 148° (Found: Br, 33·2. $C_8H_9N_2BrS$ requires Br, 32·6%).

5-*Bromo*-1-*methylaminobenzthiazole Hexabromide.*—*p*-Bromophenylmethylthiocarbamide (1·1 g.) in chloroform (10 c.c.) was gradually treated with bromine (0·7 c.c.), and the mixture refluxed until the evolution of hydrogen bromide was inappreciable (5—10 minutes). The solution was cooled in a freezing mixture; a red gum then separated which, on scratching, solidified in small, orange-red crystals of the *hexabromide*. This was dried in a vacuum over potassium hydroxide, washed with a little chloroform, and again dried; m. p. 122—124° (decomp.) (Found: Br, 76·8. $C_8H_7N_2Br_7S$ requires Br, 77·8%). The hexabromide was almost unaffected by 50 hours' exposure to moist air [Found: Br (labile), 31·3%].

5-*Bromo*-1-*methylaminobenzthiazole* was obtained from the hexabromide (1 g.) by means of sulphurous acid (10 c.c.) and sulphur dioxide and subsequent treatment with hot 2*N*-sodium hydroxide. It crystallised from alcohol–ethyl acetate in white plates, m. p. 225°, but was contaminated with a dibromo-substitution derivative which could not be removed by crystallisation (compare the purification

of 5-bromo-1-methylaminobenzthiazole; this vol., p. 1393) (Found : Br, 43·6. $C_8H_7N_2BrS$ requires Br, 32·9%).

s-p-*Bromophenylethylthiocarbamide* forms small needles, m. p. 129° (Found : Br, 31·0. $C_9H_{11}N_2BrS$ requires Br, 30·9%).

5-*Bromo*-1-*ethylimino*-1 : 2-*dihydrobenzthiazole Dibromide* (IV; R = Et).—Prepared from the thiocarbamide (1 g.) and bromine (0·65 c.c.) by the method used in the preparation of the preceding hexabromide, this *dibromide* was obtained in small, yellowish-orange, microscopic crystals, which were washed with chloroform and dried in a vacuum over potassium hydroxide; m. p. 212° (with sintering) (Found : Br, 57·4. $C_9H_9N_2Br_3S$ requires Br, 57·4%).

Reduction. The dibromide (0·1 g.), dissolved in acetic acid (50 c.c.), was shaken with a saturated aqueous solution of potassium iodide (10 c.c.), and the liberated iodine titrated with *N*/10-sodium thiosulphate [Found : Br, 38·0. $C_9H_9N_2BrS(Br)_2$ requires (Br), 38·4%].

5-*Bromo*-1-*ethylaminobenzthiazole Dibromide* (III; R = Et).—*p*-Bromophenylethylthiocarbamide (1 g.) in chloroform (10 c.c.) was brominated as in the previous case with 1·3 c.c. of bromine, and the mixture refluxed for 12—15 minutes. The stable *dibromide* crystallised, on rubbing, in deep red prisms, m. p. 140° (decomp.) (Found : Br, 58·0. $C_9H_9N_2Br_3S$ requires Br, 57·4%). On reduction with hydriodic acid as described above, it gave immediately 7·6% of bromine, but more was liberated after a short time, showing that the stable dibromide is reduced more slowly than the labile isomeride.

5-*Bromo*-1-*ethylaminobenzthiazole* was obtained by reducing either of the preceding dibromides with sulphurous acid and sulphur dioxide and crystallised from alcohol–ethyl acetate in lustrous plates or needles, m. p. 256—258° (Found : Br, 31·2. $C_9H_9N_2BrS$ requires Br, 31·1%).

s-p-*Bromophenyl*-n-*propylthiocarbamide* crystallises in needles, m. p. 120° (Found : Br, 29·6. $C_{10}H_{13}N_2BrS$ requires Br, 29·3%).

5-*Bromo*-1-n-*propylaminobenzthiazole Dibromide.*—The thiocarbamide (1·1 g.) was brominated in chloroform (10 c.c.) in the usual way, and the small, yellow crystals finally obtained were washed with chloroform and dried in a vacuum; m. p. 146° (decomp.) (Found : Br, 55·7. $C_{10}H_{11}N_2Br_3S$ requires Br, 55·7%).

5-*Bromo*-1-n-*propylaminobenzthiazole* separates from alcohol–ethyl acetate in lustrous plates, m. p. 130° (Found : Br, 30·8. $C_{10}H_{11}N_2BrS$ requires Br, 29·5%).

s-p-*Bromophenyl*-n-*butylthiocarbamide* crystallises in needles, m. p. 111° (Found : Br, 27·6. $C_{11}H_{15}N_2BrS$ requires Br, 27·85%).

5-*Bromo*-1-n-*butylaminobenzthiazole Dibromide.*—This was pre-

pared in the usual way and slowly formed in microscopic, yellow crystals, m.p. 149° (decomp.) (Found: Br, 54·1. $C_{11}H_{13}N_2Br_3S$ requires Br, 54·0%).

5-*Bromo*-1-n-*butylaminobenzthiazole* is very soluble in the ordinary solvents and separates from concentrated solutions in tufts of lustrous needles, m. p. 118° (Found: Br, 28·6. $C_{11}H_{13}N_2BrS$ requires Br, 28·1%).

s-p-*Bromophenyl*iso*butylthiocarbamide* crystallises in silky plates, m. p. 119° (yield 70—80%) (Found: Br, 27·9. $C_{11}H_{15}N_2BrS$ requires Br, 27·9%).

5-*Bromo*-1-iso*butylaminobenzthiazole Dibromide*.—This was prepared from the thiocarbamide in the usual way and obtained in shining, orange prisms, m. p. 127° (decomp.) (Found: Br, 53·8. $C_{11}H_{13}N_2Br_3S$ requires Br, 54·0%). It is very soluble in chloroform.

5-*Bromo*-1-iso*butylaminobenzthiazole* separates from alcohol–ethyl acetate in microscopic crystals, m. p. 137° (Found: Br, 29·5. $C_{11}H_{13}N_2BrS$ requires Br, 28·1%).

s-p-*Bromophenyl*-n-*amylthiocarbamide* melts at 115° and is somewhat difficult to crystallise (Found: Br, 26·9. $C_{12}H_{17}N_2BrS$ requires Br, 26·6%).

5-*Bromo*-1-n-*amylaminobenzthiazole Tetrabromide*.—*p*-Bromophenyl-*n*-amylthiocarbamide (1·1 g. in chloroform, 10 c.c.) was brominated in the usual way (0·7 c.c. Br), the solvent distilled off in a vacuum at room temperature, and the product kept in a vacuum over potassium hydroxide for 2 days; the *tetrabromide* then crystallised in orange prisms, m. p. 86° (decomp.) (Found: Br, 64·3. $C_{12}H_{15}N_2Br_5S$ requires Br, 64·5%). Its stability in moist air was of the order of that of the tetrabromides of the 1-xylidinodimethylbenzthiazoles (this vol., p. 1401).

5-*Bromo*-1-n-*amylaminobenzthiazole* crystallises from alcohol–ethyl acetate in small plates, m. p. 105° (Found: Br, 27·6. $C_{12}H_{15}N_2BrS$ requires Br, 26·7%).

s-p-*Bromophenyl*iso*amylthiocarbamide* crystallises in needles, m. p. 120° (Found: Br, 26·4. $C_{12}H_{17}N_2BrS$ requires Br, 26·6%).

5-*Bromo*-1-iso*amylaminobenzthiazole Dibromide*.—This was prepared and purified like the preceding tetrabromide and was usually obtained in ill-defined crystals, m. p. 95° (decomp.) (Found: Br, 50·7. $C_{12}H_{15}N_2Br_3S$ requires Br, 52·3%). On one occasion, however, a beautifully crystalline *dibromide* was isolated, m. p. 111° (decomp.) (Found: Br, 51·5%).

5-*Bromo*-1-iso*amylaminobenzthiazole*, prepared by reducing the dibromide, was usually resinous and crystallised from alcohol–ethyl acetate with some difficulty. The crystals, m. p. 171°, were impure (Found: Br, 29·0. $C_{12}H_{15}N_2BrS$ requires Br, 26·7%).

s-p-*Bromophenyl*-n-*hexylthiocarbamide* crystallises in small prisms, m. p. 189° (Found: Br, 25·2. $C_{13}H_{19}N_2BrS$ requires Br, 25·4%).

5-*Bromo*-1-n-*hexylaminobenzthiazole Dibromide.*—*p*-Bromophenylhexylthiocarbamide (1·2 g. in chloroform, 10 c.c.) was brominated in the usual way, and the solution concentrated in a vacuum. The red gum obtained, after standing in a vacuum over potassium hydroxide, changed to a yellow solid which could not be crystallised (Found: Br, 49·5. $C_{13}H_{17}N_2Br_3S$ requires Br, 50·7%).

5-*Bromo*-1-n-*hexylaminobenzthiazole* was obtained as a white solid which was extremely difficult to purify; m. p. 156° (Found: Br, 27·7. $C_{13}H_{17}N_2BrS$ requires Br, 25·6%).

s-p-*Bromophenyl*-n-*heptylthiocarbamide* crystallises in shining plates, m. p. 100° (Found: Br, 24·5. $C_{14}H_{21}N_2BrS$ requires Br, 24·3%).

5-*Bromo*-1-n-*heptylaminobenzthiazole Dibromide.*—This was obtained in the same way as the tetrabromide of the *n*-amyl compound, in small, yellowish-orange needles, m. p. 118—120° (decomp.) (Found: Br, 48·2. $C_{14}H_{19}N_2Br_3S$ requires Br, 49·3%).

5-*Bromo*-1-n-*heptylaminobenzthiazole* was obtained impure and with some difficulty from alcohol–ethyl acetate in microscopic crystals which became yellow and melted at 86° (Found: Br, 29·7. $C_{14}H_{19}N_2BrS$ requires Br, 24·6%).

It is hoped to examine the chemotherapeutical properties of some of these bases at an early date.

In conclusion, the authors desire to express their gratitude to Professor J. F. Thorpe, F.R.S., for his kind interest in these experiments, and to Dr. R. W. West for helpful suggestions. A part of the expense of this investigation has been defrayed by a grant from the Dixon Fund of the University of London.

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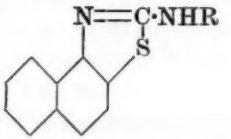
CCCXCVII.—*Aminobenzthiazoles. Part VII. The 2-Alkylamino-β-naphthathiazole System.*

By GEORGE MALCOLM DYSON, ROBERT FERGUS HUNTER, and CHARLES SOYKA.

IN the investigation of the relation between unsaturation and mobility in tautomeric systems of the aminobenzthiazole type (preceding papers) it seemed desirable, for the purpose of comparison, to examine a system consisting almost entirely of the aminothiazole phase. The 2-alkylamino-β-naphthathiazole system (I ⇌ II)

should be in this state if the alkyl group R is sufficiently large and therefore the bromination of the *s*-α-naphthylalkylthiocarbamides under the usual conditions (Hunter, J., 1925, **127**, 2023, 2270, and later papers) was studied. Unfortunately, however, owing to the

(I.)  (II.)

tendency of the thiazole nucleus in naphthathiazoles of this type to add on more than two bromine atoms (*loc. cit.*) and owing to the instability of some of the bromo-addition compounds (which partly decomposed with loss of bromine on dissolving in acetic acid), it was impossible to obtain a stability curve for the bromo-addition compounds of the alkylaminonaphthathiazole series.

On bromination in chloroform under the usual conditions, *s*-methyl- and *n*-propyl-α-naphthylthiocarbamides gave unstable *hexabromo*-addition compounds of the 2-alkylamino-β-naphthathiazoles, to which the formula III or IV (R = Me or Pr$^{\alpha}$) must be assigned,* whereas *s*-ethyl- and *n*-butyl-α-naphthylthiocarbamides were converted into *tetrabromides* (V; R = Et or *n*-C_4H_9) similar to the 1-arylaminobenzthiazole tetrabromides previously described. The

(III.) $C_{10}H_6<\begin{matrix}SBr_4^-\\NBr_2\end{matrix}>C{\cdot}NHR$ $C_{10}H_6<\begin{matrix}SBr_2\\NBr(Br_3)\end{matrix}>C{\cdot}NHR$ (IV.)

(V.) $C_{10}H_6<\begin{matrix}SBr_2^-\\NBr_2\end{matrix}>C{\cdot}NHR$ $C_{10}H_6<\begin{matrix}SBr_4^-\\NBr_2\end{matrix}>C{\cdot}NHR,HBr$ (VI.)

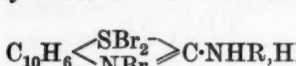
alternation of hexabromides and tetrabromides in the ascending homologous series is striking, particularly in view of the fact that α-naphthylthiocarbamide on bromination yields 2-amino-β-naphthathiazole tetrabromide (Hunter, this vol., p. 1390).

Bromination of *s-iso*butyl- and *iso*amyl-α-naphthylthiocarbamides yielded *heptabromo*-addition compounds of the 2-*iso*alkylamino-β-naphthathiazoles similar to the heptabromides of 1-*m*-toluidino-4-methylbenzthiazole (J., 1925, **127**, 2025), 2-α-naphthylamino-β-naphthathiazole (*ibid.*, p. 2270), and 1-*m*-xylidino-3 : 5-dimethylbenzthiazole (this vol., p. 1402), being doubtless the hydrobromides of the hexabromo-addition compounds (VI; R = *iso*-C_4H_9 or *iso*-C_5H_{11}).

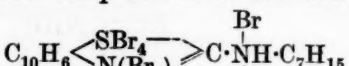
The fact that the two branched-chain alkylaminonaphthathiazoles gave rise to heptabromides is noteworthy, since the large atomic volumes of such alkyl groups would be expected to enhance the aminothiazole phase of the triad system.

* The choice between these two formulæ will be discussed in a future paper.

s-*n*-Amyl- and *n*-hexyl-α-naphthylthiocarbamides yielded *penta-bromo*-addition compounds of the 2-alkylamino-β-naphthathiazoles (VII; R = *n*-C_5H_{11} or *n*-C_6H_{13}). The former compound is the first hydrobromide of a tetrabromo-addition compound to be isolated.



(VII.)



(VIII.)

Bromination of *s*-α-naphthyl-*n*-heptylthiocarbamide in presence of a large excess of halogen gave rise to a *tetradecabromo*-addition compound of 2-*n*-heptylamino-β-naphthathiazole, which probably has the constitution (VIII). Notwithstanding its high halogen content, this compound is remarkably stable and is only slowly reduced to the heptylaminonaphthathiazole by sulphurous acid and sulphur dioxide.

The normal product of bromination of nascent 2-alkylamino-β-naphthathiazoles therefore appears to be a tetrabromide (V), which in certain circumstances is capable of adding on either bromine to give a hexabromide (III or IV), or hydrogen bromide to give a pentabromide (VII), or both of these to give a heptabromide (VI).

Experimental.

2-Methylamino-β-naphthathiazole Hexabromide (III or IV; R = Me).—*s*-α-Naphthylmethylthiocarbamide (Dyson and Hunter, *Rec. trav. chim.*, 1926, **45**, 421) (0·3 g.), dissolved in cooled chloroform (5 c.c.) was treated with bromine (0·5 c.c.) in the usual way (see previous papers), a precipitate of the bromo-addition compound being formed. The mixture was refluxed for 5 minutes, concentrated, and cooled, and the *hexabromide* was collected on porous earthenware and dried in a vacuum over potassium hydroxide for 12 hours. It formed silky, vermilion needles, m. p. 163° (decomp., blackening at 75—80°) (Found : Br, 68·2. $C_{12}H_{10}N_2Br_6S$ requires Br, 69·0%). The compound had the usual properties, losing bromine gradually on exposure to moist air, liberating iodine from dilute hydriodic acid, and being reduced by sulphurous acid and sulphur dioxide to the methylaminonaphthathiazole in the usual way (Hunter, J., 1925, **127**, 2023, 2270).

2-Methylamino-β-naphthathiazole.—The product of the preceding reduction was dried, and boiled for a short time with 2*N*-sodium hydroxide. The free *base*, after being washed and dried, separated from alcohol–ethyl acetate (1 : 1) in small, soft crystals, m. p. 193° (Found : S, 13·4. $C_{12}H_{10}N_2S$ requires S, 14·9%).

2-Ethylamino-β-naphthathiazole Tetrabromide (V; R = Et).—This was prepared from *s*-α-naphthylethylthiocarbamide (Dyson and Hunter, *loc. cit.*) (0·9 g.), chloroform (10 c.c.), and bromine (1 c.c.)

in the usual way. The *tetrabromide* separated in yellowish-brown, microscopic crystals which, after drying in a vacuum over potassium hydroxide, melted and charred at 203° (Found: Br, 57·9. $C_{13}H_{12}N_2Br_4S$ requires Br, 58·4%). It had the usual properties of these substances; on exposure to air for 12 hours, it became brown.

2-*Ethylamino*-β-*naphthathiazole* crystallised from alcohol–ethyl acetate in soft, silky needles, m. p. 218° (Found: S, 13·2. $C_{13}H_{12}N_2S$ requires S, 14·0%).

s-α-*Naphthyl*-n-*propylthiocarbamide*, prepared by condensing *n*-propylthiocarbimide (1 mol.) with α-naphthylamine (1 mol.) in alcoholic solution, crystallised in long, prismatic needles, m. p. 67° (Found: S, 12·8. $C_{14}H_{16}N_2S$ requires S, 13·2%).

2-n-*Propylamino*-β-*naphthathiazole Hexabromide* (III or IV; R = Pr^n).—This was prepared like the methyl compound (*s*-α-naphthyl-*n*-propylthiocarbamide, 1 g.; chloroform, 10 c.c.; bromine, 1 c.c.) and was obtained, by concentrating the solution, in microscopic, red crystals which sintered at 153° after drying in a vacuum (Found: Br, 66·5. $C_{14}H_{14}N_2Br_6S$ requires Br, 66·6%). The compound had the usual properties, and lost bromine on exposure to air, becoming reddish-brown. After a day, its m. p. fell to 147° (sintering).

2-n-*Propylamino*-β-*naphthathiazole* crystallised from alcohol–ethyl acetate in glistening, silky plates having a pink tinge; m. p. 242° (Found: S, 13·0. $C_{14}H_{14}N_2S$ requires S, 13·2%).

s-α-*Naphthyl*-n-*butylthiocarbamide* was obtained from *n*-butylthiocarbimide and α-naphthylamine in the usual way and crystallised from alcohol in small prisms, m. p. 98° (Found: S, 11·8. $C_{15}H_{18}N_2S$ requires S, 12·3%).

2-n-*Butylamino*-β-*naphthathiazole Tetrabromide* (V; R = *n*-C_4H_9).—*s*-α-Naphthyl-*n*-butylthiocarbamide (0·9 g.) in chloroform (10 c.c.) was treated with bromine (0·8 c.c.) as in the previous case. On concentration, the *tetrabromide* was obtained in tufts of glistening, golden needles having a pink tinge; m. p. 134° (decomp.) (Found: Br, 55·6. $C_{15}H_{16}N_2Br_4S$ requires Br, 55·5%). It had the usual properties, but showed no appreciable colour change after 48 hours' exposure to air.

2-n-*Butylamino*-β-*naphthathiazole* separated from alcohol–ethyl acetate in small, glistening prisms, m. p. 177° (Found: S, 12·0. $C_{15}H_{16}N_2S$ requires S, 12·5%).

s-α-*Naphthyl*iso*butylthiocarbamide* was obtained by the condensation of *iso*butylthiocarbimide and α-naphthylamine in alcohol, the reaction being complete after 10 minutes' boiling. The thiocarbamide crystallised in aggregates of long needles, m. p. 106° (Found: S, 12·3. $C_{15}H_{18}N_2S$ requires S, 12·4%).

2-iso*Butylamino*-β-*naphthathiazole Hexabromide Hydrobromide* (VI;

R = *iso*-C_4H_9).—This was prepared from *s*-α-naphthyl*iso*butylthiocarbamide (0·75 g.), chloroform (10 c.c.), and bromine (0·8 c.c.), an orange-yellow precipitate forming. After the mixture had been refluxed, the *heptabromide* was obtained in brown, microscopic needles, m. p. 103° (decomp.) (Found : Br, 69·7. $C_{15}H_{16}N_2Br_6S$,HBr requires Br, 68·6%). After 2 days' exposure to air, the substance became brownish-grey and melted at 243° (decomp.).

2-iso*Butylamino*-β-*naphthathiazole* separated from alcohol–ethyl acetate in crystals contaminated with resinous material; these were triturated with ether and recrystallised, and were thus obtained in small, grey prisms with a purple tinge; m. p. 242° (Found : S, 12·5. $C_{15}H_{16}N_2S$ requires S, 12·5%).

s-α-*Naphthyl*-n-*amylthiocarbamide* was prepared by boiling an alcoholic solution of *n*-amylthiocarbimide (Dyson and Hunter, *loc. cit.*) (1 mol.) and α-naphthylamine (1 mol.) for 3 hours; it crystallised in colourless prisms, m. p. 103° (Found : S, 11·2. $C_{16}H_{20}N_2S$ requires S, 11·8%).

2-n-*Amylamino*-β-*naphthathiazole Tetrabromide Hydrobromide* (VII; R = *n*-C_5H_{11}).—The preceding thiocarbamide (1·1 g.) was brominated in chloroform (10 c.c.) in the usual way. There was no precipitation on addition of the halogen and the action was less vigorous than in the previous cases. The solution was concentrated to 7 c.c. and cooled; the *pentabromide* then crystallised in glistening, silky, yellow plates, m. p. 123° (decomp.) (Found : Br, 58·9. $C_{16}H_{18}N_2Br_4S$,HBr requires Br, 59·6%). The pentabromide had the usual properties.

2-n-*Amylamino*-β-*naphthathiazole* separated from alcohol–ethyl acetate in small, glistening prisms, m. p. 107° (Found : S, 11·6. $C_{16}H_{18}N_2S$ requires S, 11·8%).

s-α-*Naphthyliso**amylthiocarbamide* was obtained in the same way as the *n*-isomeride, but the reaction was complete after 10 minutes' boiling. The thiocarbamide crystallised from alcohol in white prisms, m. p. 92° (Found : S, 11·9. $C_{16}H_{20}N_2S$ requires S, 11·8%).

2-iso*Amylamino*-β-*naphthathiazole Hexabromide Hydrobromide* (VI; R = *iso*-C_5H_{11}).—The thiocarbamide (1 g.), dissolved in warm chloroform (10 c.c.), was treated with bromine (1 c.c.), hydrogen bromide being copiously evolved and a precipitate forming. After drying in a vacuum, the *heptabromide* was obtained in small, yellow crystals having a green tinge; these sintered at 135°, blackened at 200°, and disintegrated at 222° (Found : Br, 67·5. $C_{16}H_{18}N_2Br_6S$,HBr requires Br, 67·5%). The compound had the usual properties.

2-iso*Amylamino*-β-*naphthathiazole* separated from alcohol–ethyl acetate in small, light grey, microscopic crystals having a pink tinge; m. p. 117° (Found : S, 11·0. $C_{16}H_{18}N_2S$ requires S, 11·8%).

s-α-*Naphthyl*-n-*hexylthiocarbamide* crystallised from alcohol in rosettes of minute needles, m. p. 89° (Found: S, 11·2. $C_{17}H_{22}N_2S$ requires S, 11·2%).

2-n-*Hexylamino*-β-*naphthathiazole Tetrabromide Hydrobromide* (VII; R = n-C_6H_{13}).—This was obtained from the naphthylhexylthiocarbamide (0·3 g.), chloroform (3 c.c.), and bromine (0·4 c.c.), but no precipitate formed until the solution had been heated, concentrated, and cooled; then, on rubbing, the *pentabromide* separated in shining, yellow plates, m. p. 127° (decomp.) (Found: Br, 58·9. $C_{17}H_{20}N_2Br_4S,HBr$ requires Br, 58·5%). The compound had the usual properties.

2-n-*Hexylamino*-β-*naphthathiazole* separated from alcohol–ethyl acetate in small plates having a pink tinge; m. p. 111° (Found: S, 11·0. $C_{17}H_{20}N_2S$ requires S, 11·3%).

s-α-*Naphthyl*-n-*heptylthiocarbamide* crystallised from alcohol in brilliant, flat needles, m. p. 62° (Found: S, 10·0. $C_{18}H_{24}N_2S$ requires S, 10·7%).

2-n-*Heptylamino*-β-*naphthathiazole Tetradecabromide* (VIII).—A solution of *s*-α-naphthyl-*n*-heptylthiocarbamide (0·9 g.) in chloroform (10 c.c.) was treated with bromine (0·8 c.c.) in the usual way; the shining, yellow, microscopic needles of the bromide thus obtained became green when washed with chloroform. The product was therefore suspended in chloroform and again treated with bromine; dark olive-green crystals of a *tetradecabromide* were then obtained which, after drying, charred and disintegrated at 220° (Found: Br, 79·5. $C_{18}H_{22}N_2Br_{14}S$ requires Br, 79·0%). This compound became mauve after exposure to air for 2 days.

2-n-*Heptylamino*-β-*naphthathiazole*.—The tetradecabromide was suspended in sulphurous acid and treated with sulphur dioxide for 2—3 hours. The product was collected after some time, boiled with 2*N*-sodium hydroxide, washed, dried, and crystallised from ethyl acetate–alcohol, from which the *base* separated in small, shining, purple needles, m. p. 97° (decomp.) (Found: S, 10·5. $C_{18}H_{22}N_2S$ requires S, 10·7%).

The authors desire to express their gratitude to Professor J. F. Thorpe, F.R.S., for his kind interest in these experiments, and one of them (R. F. H.) is indebted to the Trustees of the Dixon Fund of the University of London for a grant which has defrayed the cost of some of the materials.

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NOTES.

The Colour produced by the Action of Light on Concentrated Solutions of Ammonium Thiocyanate. By Emil Alphonse Werner and Kenneth Claude Bailey.

The well-known pink coloration which develops in ammonium thiocyanate, or in a concentrated aqueous solution of the salt, on exposure to light has been recently investigated by Holmes (this vol., p. 1690), who is disposed to attribute it to insoluble sulphur aggregates of sub-microscopic size produced in the irreversible change $NH_4SCN \rightarrow NH_4CN + S$ (sol).

In view of the following facts, however, it seems probable that the dissociation of the salt into ammonia and thiocyanic acid is the phenomenon which is primarily responsible for the result.

(*a*) Ammonium thiocyanate, or a strong solution thereof, which has developed a pink colour invariably shows an acid reaction, and neutralisation with ammonia causes the pink coloration to disappear.

(*b*) A colourless solution of potassium thiocyanate, which yields no colour to ether or amyl alcohol, gives, on addition of hydrochloric acid, a pink colour which is readily extracted from the solution by these solvents, a phenomenon already discussed by one of us (Bailey, *Proc. Roy. Irish Acad.*, 1924, **37**, 6).

(*c*) The coloration produced by insolation of ammonium thiocyanate appears to behave in a similar manner to the pink coloration produced as in (*b*). It can be extracted from aqueous solution by ether, but is not removed by carbon disulphide or benzene, solvents which might be expected to remove sulphur and thus extract or destroy the colour if due to the cause advanced by Holmes.

The solvents—amyl, butyl, and benzyl alcohols, amyl acetate, ether, diphenyl ether, and nitrobenzene—which gave a pink extract of thiocyanic acid from an aqueous solution of potassium thiocyanate acidified with hydrochloric acid all contain oxygen, whereas no extraction was obtained with amylene, ethylene dibromide, chloroform, carbon tetrachloride, carbon disulphide, benzyl chloride, benzene, toluene, or turpentine.

(*d*) A pink solution of thiocyanic acid in amyl alcohol, on exposure in a glass vessel to the action of light for a long time, gradually lost its colour, a precipitate was produced, and hydrocyanic acid was detected in the liquid. The development of hydrocyanic acid occurs, therefore, at a second stage in the process.

(*e*) Aqueous solutions of thiosulphuric acid and the thionic acids liberate colloidal sulphur but show no pink coloration.